SYNTHESIS OF ALTERNATING COPOLYMERS AND OPTICALLY ACTIVE POLYMERS VIA DIELS-ALDER AND ENE REACTIONS USING N-SUBSTITUTED TRIAZOLINEDIONES

By

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To my parents:

Taghi and Khanum-Bozorg Mollakpour
who through their love, encouragement, and sacrifices
gave their six children the opportunities they never had

To my sisters:

Mehterum, Ehteruhm, and Ahzem

To my brothers:

Hadi and Majid

To my wife:

Mina

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SYNTHESIS OF ALTERNATING COPOLYMERS AND OPTICALLY ACTIVE POLYMERS
VIA DIELS-ALDER AND ENE REACTIONS
USING N-SUBSTITUTED TRIAZOLINEDIONES

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Chairman: Dr. George B. Butler
Major Department: Chemistry

The aim of the first part of this investigation was the selection of a suitable plasticizer for the development of a new elastomeric impression material system using bis-triazolinediones as crosslinking agents. Isoeugenol was selected for this study. It was converted to its methyl urethane derivative. In order to evaluate the reactivity of the methyl urethane derivative of isoeugenol with bis-triazolinediones, two model compounds were prepared by reaction of 4-Ph and 4-Me-1,2,4-triazoline-3,5-diones with this compound. The products were formed by a successive two-step Diels-Alder-ene reaction. Their structures were determined by using ^{1}H NMR, ^{13}C NMR, IR and mass spectra.

The reaction between the methyl urethane of isoeugenol and bis-triazolinediones yielded alternating copolymers with Diels-Alder-ene

repeating unit. These copolymers are soluble in polar solvents. Intrinsic viscosities of the new copolymers were measured in N,N-dimethylformamide, and were found to be in the range of 0.20 dl/g. The copolymer with R = diphenylmethane showed very high thermal stability.

The purpose of the second part of this research was to synthesize optically active polymers using N-chiral-triazolinediones via the ene reaction. Thus, optically active pure S-(-)- and R-(+)-4-(α-methylbenzyl)-1,2,4-triazoline-3,5-diones were synthesized using optically pure amine by a series of chemical transformations. S-(-)CTD was found to be quite stable in solvents such as CH_2Cl_2, toluene and acetone, and it decomposes slowly in solvents such as DMF, DMSO and THF. The pseudo first-order kinetics for such a decomposition were studied.

The ene reaction of S-(-)CTD with propylene was carried out in order to obtain a model compound for further use in the study of modification of polydienes. Bromination of this compound with a solution of Br_2 in carbon tetrachloride furnished the desired dibromide adduct. An X-ray diffraction analysis of a single crystal of this compound was determined. The absolute configuration was found to be S, and intramolecular hydrogen bonding was observed.

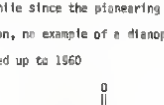
1,4- and 1,2-Polydienes were modified with S-(-)- and R-(+)CTDs. The resulting polymers are optically active. The intrinsic viscosities of the modified polymers at various percents of conversion were measured. The intrinsic viscosity decreases as percent conversion increases. This is due to intramolecular interaction. Evidence for intra- and intermolecular associations was given by X-ray analysis of the model compound as well as by IR spectroscopy.

CHAPTER I

INTRODUCTION

General Background

The cycloaddition reactions of compounds containing electron-poor nitrogen to nitrogen double bonds as dienophiles have been extensively studied.[1] Although diethyl azodicarboxylate, 1, has been used as a dienophile since the pioneering work of Diels[2] on the Diels-Alder reaction, no example of a dienophile having a cis-azo-linkage had been reported up to 1960.



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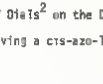
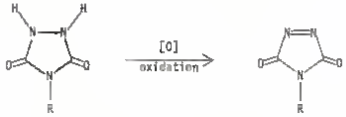


2a, R = CH_3

2b, R = C_6H_5

4-Phenyl-1,2,4-triazoline-3,5-dione (PhTD), 2b, (the N-phenyl-imide of azodicarboxylic acid) was reported as long ago as 1894 by Thiele[3] and later by Stolle[4] in 1912. Both obtained it by oxidation of 4-phenylurazole, 3, but were not able to isolate it. The oxidation can be accomplished with a wide variety of oxidizing reagents. Thiele used lead peroxide in cold dilute sulfuric acid.[3] Stolle oxidized heavy metal salts of the urazoles with iodine.[4] Cookson used



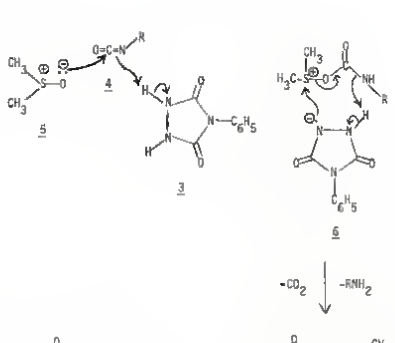
3, R = C_6H_5 2b

t-butylhypochlorite in acetone;[5] Gillis and Hagarty employed lead tetra-acetate in methylene chloride,[6] bromine[7] and fuming nitric acid,[8] manganese dioxide, calcium hypochlorite and N-bromosuccinimide will also effect the oxidation of urazoles.[9] However, all of the above mentioned reagents produce by-products which either destroy or are difficult to remove from the sensitive triazolinediones.

In 1966, Stickler and Pirkle[10] discovered that the gaseous dinitrogen tetroxide is the most effective oxidizing agent that also gives high yield and purity. This was accomplished by passing gaseous dinitrogen tetroxide into a slurry of the urazole precursor in cold methylene chloride (-10 to -5°C), rapid formation of the corresponding triazolinedione resulted. Purification was performed by evaporation of the solvent followed by sublimation at reduced pressure which furnished the crystalline triazolinedione.

Moore and coworkers[11] recently reported the oxidation of urazole and subsequent reaction in situ. Oxidation was achieved via an activated isocyanate, 4, such as p-toluenesulfonyl isocyanate in dimethyl sulfoxide, 5. The proposed mechanism for this oxidation is shown in Scheme I. The extent of oxidation was determined spectrophotometrically.

Scheme I

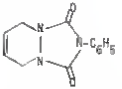


Although a series of 4-substituted triazolinediones have been prepared in this fashion and isolated, the parent compound (R=H) has never been isolated, possibly due to its extremely high reactivity. It was first synthesized by Stolle,[4] who was not able to isolate it. DeAmezua and coworkers[12] prepared the compound at low temperature and trapped it *in situ* with several dienes via the Diels-Alder reaction.

Herwah and Fantazier[13] synthesized this compound by oxidation of urazole with dinitrogen tetroxide and lead tetraacetate and trapped it with dienes. They also investigated the decomposition product by oxidizing urazole with dinitrogen tetroxide gas at room temperature and collecting the gases evolved, such as nitrogen, carbon dioxide and cyanuric acid.

4-Substituted-1,2,4-triazoline-3,5-diones are very sensitive to acid, base, alcohol, light, heat, and moisture, therefore, they should be kept in tight bottles away from light and moisture. These compounds are very reactive dienophiles as well as enophiles. The chemistry of triazolinediones, with the exception of their enhanced reactivity due to cis-configuration, is similar to that of diethyl azodicarboxylate and other α-carbonyl azo compounds.[13-22] It has been reported that PhTD is 1000 times more reactive in the Diels-Alder reaction with 2-chlorobutadiene than tetracyanoethylene (TCNE)[23] and 2000 times more reactive than maleic anhydride.[24] 4-Methyl-1,2,4-triazoline-3,5-dione (4-MeTD), 2a, has been reported to be at least 30,000 times more reactive toward cyclohexene than its open chain analogue, diethyl azodicarboxylate.[25]

Cookson and coworkers[5,26] investigated the Diels-Alder reaction of 4-PhTD with butadiene and cyclopentadiene at low temperature which resultad in the adducts 8 and 9, respectively. After this work was published, an extensive amount of research related to Diels-Alder reaction of triazolinediones with various dienes was reported.[27-32]



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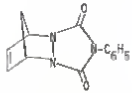

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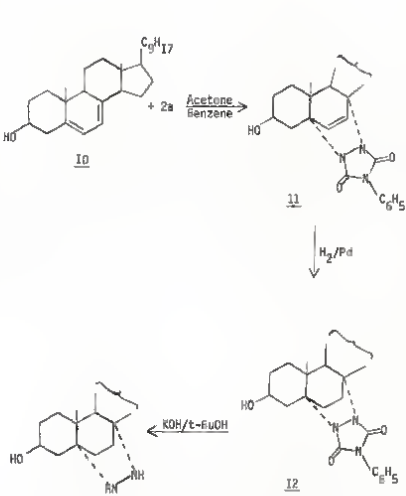
Although ergosterol, 10, reacts slowly with maleic anhydride,[33] and its reaction with diethyl azodicarboxylate[34] leads to the hydrogen abstraction-addition reaction (the "ene" reaction), 4-PhTD (2a) reacts with ergosterol via the Diels-Alder reaction[27] at 0°C. This reaction is fast and leads to the incorporation of the hydrazo bridge into ring B of ergosterol. The complete chemical transformations which give the hydrazo derivative are shown in Scheme II. The hydroxyl group of ergosterol also could react with 4-PhTD, but it was not mentioned in this paper.

The cycloaddition reaction of 4-phenyl-1,2,3-triazoline-3,5-dione, 2a, with cyclooctatetraene, 14, was first reported by Cookson and coworkers in 1967.[35] The reaction was performed at 100°C in dioxane and afforded exclusively the normal adduct 15 in a 32% yield. Reinvestigation of this reaction under the same conditions by Evnin and coworkers[36] revealed that the adducts 16 and 17 are formed in about a 1:1 ratio on the basis of the NMR spectrum of the crude mixture. They also found that this reaction at 25°C in an acetone-benzene mixture gives adduct 17 in a 30-35% yield and adduct 16 in less than 0.5% yield.

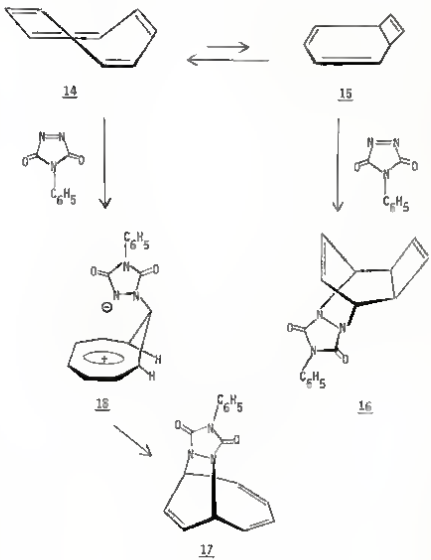
Scheme II



Later, Huisgen et al.[37] investigated the reaction at various temperatures and explained the formation of two adducts, I6 and I7, by way of two different isomers, I4 and I5, of cyclooctatetraene as is shown in Scheme III. Since the boat conformation, I4, does not provide a

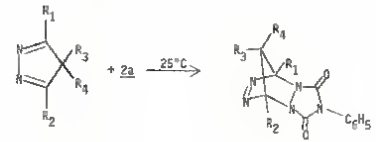
planar 1,3-diene system suitable for the Diels-Alder reaction due to the hindrance to conjugation of the localized double bonds, it was presumed that the formation of adduct 17 occurs via the homotropylium Zwitterion 18.

Scheme III



The Diels-Alder reaction of isopyrazoles 19 with 4-PhTD was studied by Arnold et al.[36,35] A specific example of this reaction is shown in Scheme IV. This reaction occurs at room temperature, and

Scheme IV



$R_1 = R_2 = R_3 = R_4 = CH_3$

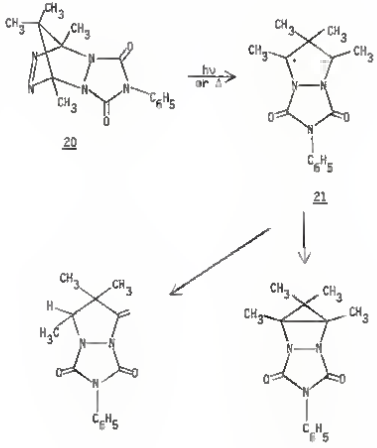
19

20

the azo adduct 20 is crystalline and can be readily isolated. It is also light sensitive, but can be stored for many months in the dark at room temperature. This type of azo adduct will decompose thermally and photochemically via loss of nitrogen to yield a 1,3-diradical, 21, which either disproportionates intramolecularly to 22 or closes to form the bicyclo [2.1.0] pentane derivatives 23, as shown in Scheme V. This Diels-Alder reaction is interesting since one could synthesis co-polymers containing azo groups in their repeating unit by employing the reaction of bis-triazolinediones with bis-isopyrazoles.

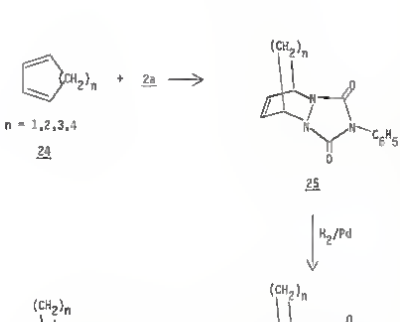
4-PhTD, 2a, was treated with a wide variety of dienes to yield adducts of structure 25. These compounds were further converted to cis-ezoxy alkanes 27 by a series of chemical reactions[40] as shown in Scheme VI.

Scheme V



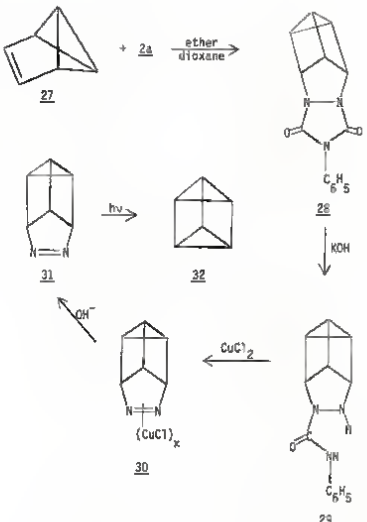
20 21 22 23

Scheme VI



Prismane, 32, is a compound with molecular formula C_6H_6 in which six carbon-hydrogen units are disposed at the corners of a triangular prism. Ladenburg[41a] first proposed its structure for benzene 114 years ago. This compound was prepared by Katz and Acton[41b] by using the cycloaddition reaction of benzvalene, 27, with 4-PhTD, 2a, followed by other chemical transformations as outlined in Scheme VII. The mechanism of the formation of adduct 26 was also investigated by the same

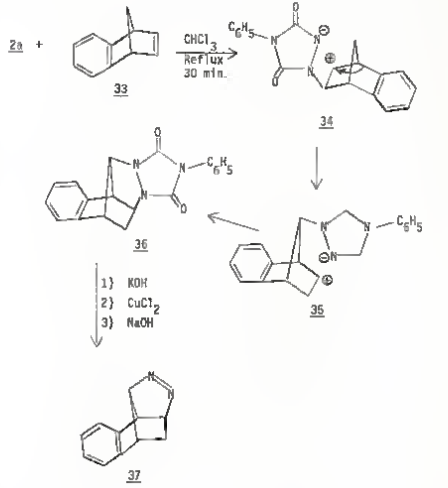
Scheme VII



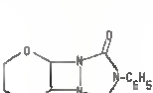
authors.[42] Prismane, 32, was isolated in 1 8% yield by the above procedure. It is an explosive, colorless liquid and is stable at room temperature, but at 90°C in toluene-d_8 it decomposes with a half-life of 11 hours to benzene.

The cycloaddition reaction of a strained bicyclic olefin with 4-PhTD was used to generate the unknown tricyclic azoalkane[43] 37. The formation of the cycloadduct was proposed to proceed via dipolar addition, followed by rearrangement as is shown in Scheme VIII.

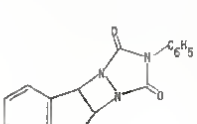
Scheme VIII



The 2+2 cycloaddition reaction of 4-PhTD with dihydro-1,4-dioxime and indene was observed by Von Gustorf and coworkers.[44] The cycloadducts 38 and 39 were isolated. The indene reaction pathway was thought to be polar in nature, as the proposed 1,4-dipolar intermediate was trapped with water.

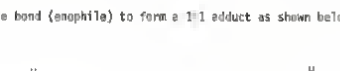


38



39

As previously mentioned, triazolinedione is also an extremely powerful enophile and can participate in the "ene" reaction. The ene reaction, first recognized and systematically investigated nearly 40 years ago by Alder,[45] usually involves the thermal reaction of an olefin containing an allylic hydrogen (ene) with an electron-deficient multiple bond (enophile) to form a 1:1 adduct as shown below:



This reaction is structurally related to the Diels-Alder reaction[46] and [1,5]-sigmatropic shifts[47] in that they all have a cyclic 6$\overline{e}$ transition state.

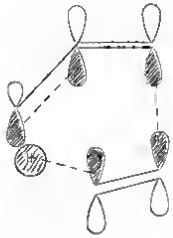
Mechanistic and preparative aspects of the ene reaction were comprehensively reviewed by Hoffmann in 1964.[48] The ene reaction can occur in a concerted fashion as well as stepwise via biradical or ionic intermediates.

When the geometry is such that the enophile can simultaneously attack the π electrons and the allylic hydrogen atom of the ene component, a facile reaction appears to take place via a concerted mechanism involving a cyclic transition state.[48] The most likely geometry of approach for the component of an ene reaction is shown (40).

40

The concerted ene reaction is thermally allowed, its transition state, 41, is aromatic in the sense that it is a Huckel system and involves a suprafacial interaction of six electrons (four from the π bonds and two from the σ bond). Using the general terminology of Woodward and Hoffmann, it can be regarded as a σ2S + π2S + π2S reaction.[49]

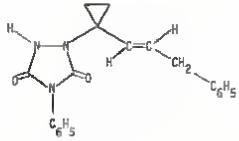
The ene reaction of 4-methyl-1,2,4-triazoline-3,5-diene with some monoolefins having allylic hydrogens was first reported by Pirkle and Stickler.[25] Pasto and Chen[50] investigated the ene reaction between



41

σ2S + π2S + π2S

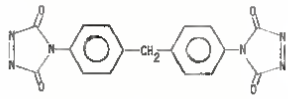
4-PhTD and (4-phenylbutylidene)-cyclopropane and obtained the adduct 42



42

A highly reactive bifunctional enophile, bis(p-3,5-dioxa-1,2,4-triazolina-4-ylphenyl)methene, 43, was first synthesized by Saville.[51] The ene reaction of this compound with different types of allylic

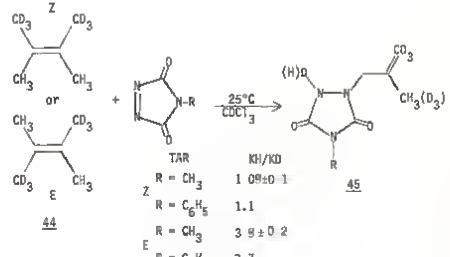
olefins (e.g., trans-2-butene, 2-methyl pent-2-ene) was studied, and relatively polar bis-ene-adducts were formed in a few seconds. He also studied the addition of this compound to a solution of natural rubber which resulted in instant gelation due to crosslinking.

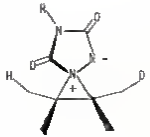


43

Green and Seymour[52] have shown that 4-substituted triazoline-diones (4-R-TD's) react with (Z) and (E)-2,3-bis-(trideuterio methyl)-2-butene, 44, to yield the ene adduct 45. Using the product isotope effect, they proposed an ionic intermediate, designated an aziridinium imide, 46, as shown in Scheme IX.

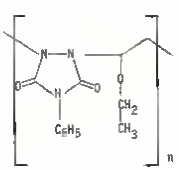
Scheme IX



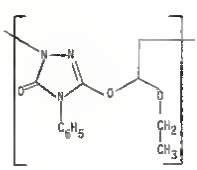


46

Butler and coworkers[53-62] used 4-R-TD's and bis-triazolinediones as dienophiles as well as enophiles. Butler, Guilbault and Turner[53] studied the reaction of 4-R-TD's with vinyl ethers and obtained the low molecular weight copolymers containing repeating units 47 and 48, formed via a 1,4-dipolar pathway. The evidence presented for the existence of the 1,4-dipolar intermediate 49 was based on the fact that it was trapped via a cycloaddition reaction with alkyl ketones,[54] which resulted in a novel 1,3,4-tetrahydrooxadiazine ring structure, 50. This intermediate also can disappear via ring closure to yield the diazetidine 51 as shown in Scheme X.

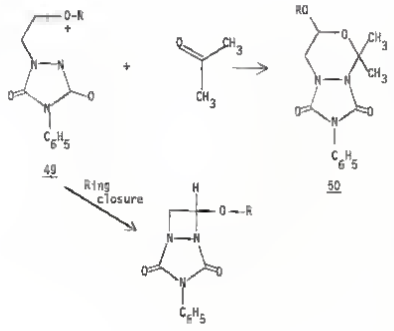


47



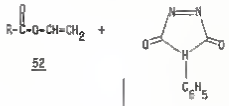
48

Scheme X

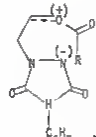


Vinyl esters were expected to react with 4-PhTD in a similar manner as vinyl ether, thus, Wagener, Turner and Butler[55] investigated the reaction of 4-PhTD with vinyl esters as shown in Scheme XI. An unexpected product, 54, was observed which was explained satisfactorily via an intramolecular rearrangement of the Zwitterion[55-58] 53 (route e). In the case of vinyl acetate, the product distribution via routes a, b and c was found to be 7, 9 and 84%, respectively. This 1,4-dipolar rearrangement was later used by Wagener, Matyjaszewski and Butler[57,58] as a propagation pathway in copolymerizations of bistriazolinediones with divinyl esters and other bis-enol esters. An example of such a copolymerization is given in Scheme XII.

Scheme XI



52 + 2a

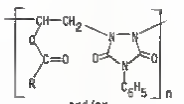


53

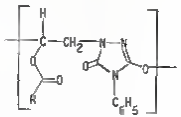
(a) 1,4-dipolar coupling

dipolar rearrangement

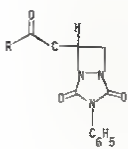
(b) diazetidine



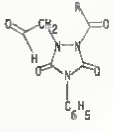
and/or



56 7%

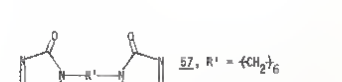


55 5%



54 84%

Scheme XII



57, R' = $-(CH_2)_6-$

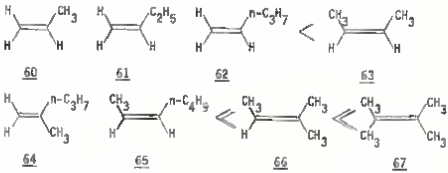
43, R' = $-\langle\bigcirc\rangle-CH_2-\langle\bigcirc\rangle-$

+

58

59

The structures of the products and the kinetics of the ene reaction between 4-R-TD's and various alkenes were also investigated by Ohashi et al.[59] and Ohashi and Butler[60] The rates of the ene reaction of 4-PhTD with various alkenes were observed to follow the order

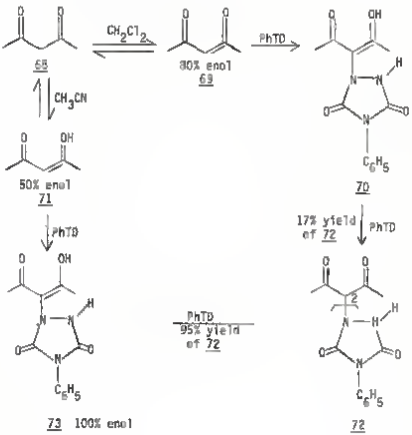


60 61 62 63

64 65 66 67

Williams and Butler[61,62] studied the reaction of 4-PhTO with β-dicarbonyl compounds as shown in Scheme XIII.

Scheme XIII



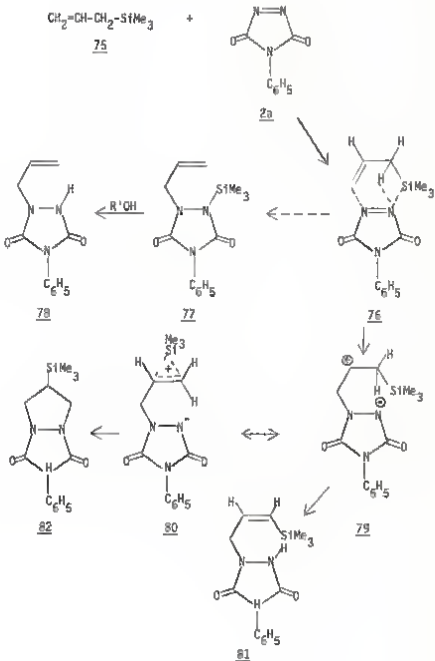
The above reaction is fast at room temperature and yields both 1:1 adduct 73 and 2:1 adduct 72. The 1:1 adduct showed a dramatic stabilization of the enolic tautomer in comparison to the original β-dicarbonyl compound. According to the above reaction, it is apparent that β-dicarbonyl compounds are bifunctional toward the addition reaction with triazolinedione. Thus, a copolymerization reaction was performed by the same authors, and an alternating copolymer with repeating unit 74 was synthesized.

74

Ohashi, Ruch and Butler[63] recently showed that trimethylallylsilane, 75, reacts with 4-PhTD to yield the three products 78, 81 and 82. The temperature and solvent effects were studied. The reaction is outlined in Scheme XIV.

They found that in benzene, the least polar solvent used, the relative yields of 81 and 78 were 75% and 9%, respectively, while in the most polar solvent, acetonitrile, the yields were 28% and 67%, respectively. The effect of temperature on the relative yields of

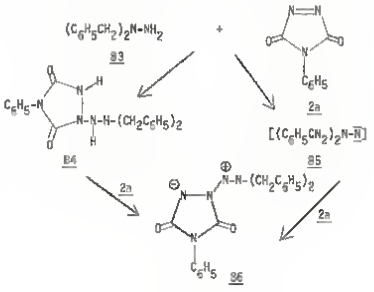
Scheme XIV



the adducts was also observed. The relative ratio of the normal ene reaction products increases as a result of increasing temperature. All products were identified by ^{1}H NMR, ^{13}C NMR and mass spectrometry. The authors concluded that the reaction mechanism should be ionic and proposed a Zwitterionic intermediate, 79. They also mentioned that in polar solvents, the intermediate would be more stable and would therefore form more easily. At high temperatures, this intermediate would be less stable.

4-R-TD's have also been used as oxidizing reagents. Cookson et al.[64] reported the oxidation of alcohols to aldehydes and ketones with 4-PhTD. This reaction takes place at room temperature over a few hours and gives ketones or aldehydes in high yield. Dibenzyl hydrazine, 83, can be oxidized using 4-PhTD as an oxidizing agent to yield N-nitrene, 85, which then can react with a second molecule of 4-PhTD to yield an azimine,[65,66] 86 (Scheme XV)

Scheme XV



Research Objectives

This work can be divided into two related parts which employ mono as well as bis-triazolinediones as dienophiles and enophiles.

The first part of this study concerns the selection of a plasticizer for the development of a new elastomeric impression materials system using bis-triazolinediones as crosslinking agents. The objectives of this study were as follows:

1. Synthesis and characterization of model compounds by the reaction of 4-Ph, MeTD's with the selected plasticizer.

2. Evaluation of the reactivity of this plasticizer with bis-triazolinediones which could lead to the formation of new alternating copolymers, followed by a study of their physical properties.

The second part of this study concerns investigation of the reaction of optically active triazolinediones with polydienes. The objectives of this study were as follows:

1. Synthesis of the N-4-chiral-substituted triazolinediones.

2. Preparation of model compounds by the ene reaction of chiral triazolinediones with alkenes having allylic hydrogens.

3. An X-ray crystallography study on the model compound to confirm its structure, absolute configuration and extent of hydrogen bonding.

4. Use of chiral triazolinediones to introduce optical activity into polydienes and a study of their physical properties. A possible application of such modified polymers would be as an optically active ion-exchange material for resolution of racemates.

CHAPTER II

EXPERIMENTAL

General Information

Optical rotations were measured by either a Rudolph Research Autopol III Automatic or a Perkin-Elmer Model 141 Polarimeter at 25°C (RT). All concentrations are reported in mg/ml. Specific rotations were calculated from the following equation.

$$[\alpha] = \frac{\theta}{l \times c}$$

where $[\alpha]$ = specific rotation (degrees), θ = observed rotation (degrees), l = pathlength (decimeters), and c = concentrations (g/ml of solution).

All temperatures are uncorrected and are reported in degrees centigrade. Melting points were determined in open capillary tubes using a Thomas-Hoover melting point apparatus. Pressures are expressed as millimeters (mm) of mercury. Elemental analyses were performed by the University of Florida, Department of Chemistry, Gainesville, Florida, and Atlantic Microlabs, Inc., Atlanta, Georgia.

Low resolution mass spectra (LRMS) and high resolution mass spectra (HRMS) were recorded on an Associated Electronic Industries (AEI) Model MS-30 spectrometer.

Intrinsic viscosities were measured by standard procedures using a Cannon-Ubbelohde semimicro viscometer (dilution viscometer).

Number average molecular weights ($\bar{M}_n$) of polymers were determined by membrane osmometry (MO) on a Wescan Model 230 Recording Membrane Osmometer Apparatus.

Differential Scanning Calorimetry data for polymers were taken on a Perkin-Elmer DSC 1B, all data on thermal transitions are reported in degrees centigrade and are uncorrected.

Infrared (IR) spectra were recorded on a Perkin-Elmer 281 Infrared Spectrophotometer. The observed frequencies are expressed in wavenumbers (cm^{-1}) using the 1601 cm^{-1} line of a polystyrene film as a standard. Spectra of oils and liquids were obtained neat as a smear on sodium chloride or potassium chloride plates, and those of solids were performed by using Nujol Mulls or KBr pellets. Vibrational transitions frequencies are reported in wavenumbers (cm^{-1}), with the intensity of the bands being assigned the following classifications: weak (w), medium (m), shoulder (sh), strong (s), broad (br).

Proton nuclear magnetic resonence (NMR) spectra (60 MHz) were recorded on a Varian EM-360L spectrometer. Carbon-13 (25.0 MHz) and 100 MHz proton NMR spectra were obtained on a Jeol JNM-FX-100 instrument. ^1H NMR (300 MHz) and 75 MHz carbon-13 spectra were determined on a Nicolet NT-300 instrument. Chemical shifts are given in parts per million (ppm) on a δ scale downfield from tetramethylsilane (TMS) or solvent peaks [dimethyl sulfoxide-d_6 (DMSO-d_6) = 2.49, ^1H; 39.5, ^{13}C or chloroform-d ($CDCl_3$) = 7.24, ^1H, 77.0, ^{13}C].[67] Multiplicities of proton and off-resonance decoupled carbon-13 resonances are designated as singlet (s), doublet (d), triplet (t), quartet (q), pentet (p), multiplet (m), or bread (br).

Ultraviolet and visible spectra were measured with a Perkin-Elmer 330 spectrophotometer.

Reagents and Solvents

Reagents were purchased from Fisher Scientific Co., Aldrich Chemical Co., or Mallinkrodt, Inc., unless otherwise noted. Deuterated NMR solvents were obtained from Merck & Co., Inc., and Aldrich Chemical Co. All gaseous reagents were obtained from Matheson Co.

All solvents used for general application were of reagent grade or ACS grade quality. For special purposes, purification of solvents was carried out by following procedures reported in the literature.[68] Thus, dimethyl formamide (DMF) was allowed to stand over potassium hydroxide pellets overnight and was distilled from calcium oxide at 60°C under reduced pressure, toluene was refluxed over calcium oxide for a period of 12 hours, then was distilled at atmospheric pressure.

Synthesis of 4-Substituted-1,2,4-triazoline-3,5-diones

Ethyl hydrazine carboxylate[6,69]

Into a 1000 ml three-necked round-bottomed flask was placed 156.25 g (2.0 moles) of hydrazine monohydrate (64% in H_2O) and 236 g (243 ml, 2.0 moles) of diethylcarbonate. The mixture turned to a milky solution. The flask was shaken vigorously to mix the two liquids. After about 2 minutes, the milky emulsion became warm, shaking was continued until a clear solution was obtained (approximately 10 minutes), and the flask was then fitted with a water-cooled condenser attached to a drying tube containing calcium chloride and heated at reflux for 4.5 hours. After cooling, the clear solution was transferred to a 500 ml round-bottomed flask and distilled through a 15 cm

vigreux column under reduced pressure. By-products (206 ml) were collected (18 mm, 80°C). The product was a colorless liquid, 176.72 g (85.0%), b.p. 102-103°C at 18 mm Hg. The clear liquid solidified on standing to a white solid, m.p. 44-46°C (lit.[6] 45-47°C).

IR (neat): 3340 (s), 2988 (m), 2940 (w), 1715 (s), 1635 (m), 1510 (s), 1405 (m), 1380 (w), 1370 (w), 1290 (s), 1185 (s), 1068 (s), 930 (w, br), 880 (w), 775 (w) cm^{-1}.

^1H NMR (DMSO-d_6, TMS): δ 1.16 (t, 3H, J = 7.0 Hz), 4.01 (q, 2H, J = 7.0 Hz), 4.01 (s, 2H, NH_2 peak is exactly in the middle of quartet, so both are reported here at 4.01 ppm), 8.04 (s, br, 1H).

1-Ethoxycarbonyl-4-phenylsemicarbazide[5,69,70]

Into a 1000 ml three-necked round-bottomed flask equipped with a constant pressure dropping funnel, a mechanical stirrer, and reflux condansar fittad with a drying tuba containing silica gel was chargad 52.0 g (0.500 mole) of ethyl hydrazina carboxylate (athyl carbazata) and 550 ml benzane. The solution was cooled in an ice-water bath to about 10°C, and tha stirrer was started. To the solution was added dropwisa 59.7 g (55 ml, 0.50 mola) of phenylisocyanate over a paried of 40 minutes. A whita precipitata formed after about one-half of tha isocyanate had been added. After the addition was complete, tha ica bath was removed, and the mixture was stirred at room temperature for 2 1/2 hours, than was heatad by means of a heating mantla under reflux for 2 hours. At the and of the refluxing period, tha slurry mixtura was allowed to cool to room temparature, and the white solid was collectad by suction filtration, washed with 500 ml of benzene, and then dried in a vacuum desiccator for 24 hours, yielding 104.0 g (93%); m.p. 146-148°C (lit.[69] 154-155°C).

IR (KBr) 3360 (s), 3220 (s), 3047 (m), 2980 (w), 1710 (s), 1670 (s), 1600 (s), 1540 (s), 1500 (m), 1475 (m), 1440 (m), 1370 (w), 1315 (m), 1230 (s), 1058 (m), 1020 (m), 890 (m), 750 (m), 690 (m) cm^{-1}

^1H NMR (DMSO-d_6, TMS): δ 1.19 (t, 3H, J = 7.0 Hz), 4.07 (q, 2H, J = 7.0 Hz), 7.19 (m, 5H), 8.01 (s, 1H), 8.73 (s, 1H), 8.93 (s, 1H)

^{13}C NMR (DMSO-d_6, TMS, int. ref. DMSO-d_6): δ 14.55, 60.55, 118.50, 121.87, 128.59, 139.70, 155.64, 157.00.

4-Phenyl Urazole[69,70]

1-Ethoxycarbonyl-4-phenylsemicarbazine (44.6 g, 0.20 mole) was placed in a 500 ml Erlenmeyer flask, and 100 ml of 4 M KOH was added. The suspension was warmed on a hot plate and stirred by means of a magnetic stirrer for 1.5 hours. Then, 80 ml of 4 M KOH was added to make sure that the reaction had taken place to a large extent. The hot solution was filtered by suction filtration. The filtrate was cooled in an ice bath and then acidified with concentrated hydrochloric acid (about 50 ml). A white solid was precipitated, filtered, and then dried in a vacuum oven at room temperature to yield 31.50 g (89.0%) of product. Recrystallization from hot water (about 300 ml) furnished a white crystalline compound, m.p. 214-215°C (lit.[69] 209-210°C)

IR (KBr): 3410 (w), 3140 (s, br), 1780 (sh), 1680 (s), 1600 (w), 1495 (s), 1440 (s), 1290 (w), 1225 (w), 1115 (m), 1070 (w), 1030 (w), 1010 (w), 910 (w), 775 (s, br), 690 (s), 625 (s) cm^{-1}.

^1H NMR (DMSO-d_6, TMS): δ 7.45 (m, 5H), 10.40 (s, br, 2H).

^{13}C NMR (DMSO-d_6, TMS, int. ref. DMSO-d_6): δ 126.50, 127.81, 128.98, 132.05, 153.69.

4-Phenyl-1,2,4-triazoline-3,5-dione[10,69]

Into a 500 ml three-necked round-bottomed flask equipped with a gas inlet tube and a magnetic stirring bar was placed 5.0 g (0.034 mole) of 4-phenyl urazole, 350 ml of methylene chloride, and 60.0 g of anhydrous sodium sulfate. The suspension was stirred by a magnetic stirrer and cooled to -5°C with an ice-salt bath. Gaseous dinitrogen tetroxide was bubbled slowly through the solution for 15 minutes. After a few minutes, a deep-red color appeared. The temperature was kept below 0°C. The red solution was allowed to stir for 30 more minutes, then was filtered. The excess N_2O_4 was removed with dry nitrogen gas (about 3 hours). Methylene chloride was removed by rotary evaporation to give 5.25 g (88.5) of crystalline red solid; m.p. 172-173°C soft, 187-197°C (dec) [lit.[69] 165-175°C (dec)].

Elemental analysis calculated for $C_8H_5N_3O_2$: C, 54.86; H, 2.88; N, 23.99. Found: C, 54.92; H, 2.93; N, 24.00.

IR (KBr): 3540 (w), 3060 (w), 1755 (s, br), 1620 (w), 1593 (m), 1525 (m), 1500 (m), 1450 (w), 1395 (s), 1315 (w), 1285 (m), 1173 (s), 1070 (m), 1025 (m), 985 (w), 910 (w), 892 (m), 765 (m), 720 (s), 670 (s), 605 (m) cm^{-1}.

1-Ethoxycarbonyl-4-methylsemicarbazide[10]

Into a 300 ml three-necked round-bottomed flask fitted with a mechanical stirrer, an addition funnel, a thermometer, and a water-cooled condenser attached to a drying tube containing silica gel was placed 20.85 g (0.197 mole) of the ethylcarbazate and 125 ml of benzene. Stirring was started, and the solution was cooled to 10°C. To this mixture, a solution of 11.25 g (0.197 mole) of methyl isocyanate

in 50 ml of benzene was added dropwise over a period of 15 minutes through the addition funnel, with the temperature being kept between 10-20°C. A white precipitate formed. The slurry mixture was stirred at room temperature for 3 hours. The white solid was filtered, washed with cold benzene, then dried in a vacuum desiccator for 24 hours to yield 30.70 g (96.5%) of product, m.p. 141.5-143°C.

IR (KBr): 3320 (s), 3220 (s), 3040 (m), 2990 (m), 2940 (w), 1720 (s), 1660 (s), 1575 (s), 1540 (s), 1460 (w), 1440 (w), 1410 (m), 1370 (w), 1285 (s), 1225 (s), 1140 (m), 1050 (s), 915 (w), 880 (w), 755 (w), 680 (m, br) cm^{-1}.

^1H NMR (DMSO-d_6, TMS): δ 1.18 (t, 3H, J = 7.2 Hz), 2.56 (d, 3H, J = 4.4 Hz), 4.03 (q, 2H, J = 7.2 Hz), 6.29 (q, 1H, J = 4.4 Hz), 7.74 (s, 1H), 8.73 (s, 1H).

^{13}C NMR (DMSO-d_6, TMS, int. ref. DMSO-d_6): δ 14.60, 26.29, 60.50, 157.05, 159.05.

4-Methyl Urazole[10]

Into a 125 ml Erlenmeyer flask was added 10.0 g (0.0620 mole) of 1-ethoxycarbonyl-4-methylsemicarbazide and 23.0 ml (0.0896 mole) of 4M potassium hydroxide. The mixture was stirred by a magnetic stirrer and warmed (60-70°C) for about 30 minutes. A pale-yellow solution was obtained, which was cooled in an ice bath and acidified with concentrated hydrochloric acid (about 8 ml is required). A white solid formed, which was filtered using suction filtration, and then dried in a vacuum oven at 104°C for 2 hours. The mother liquor was evaporated to 50% of its volume on a rotary evaporator to obtain more white solid. The additional 4-methyl urazole recovered was combined with

that previously obtained, making the total weight 6.45 g (90.3%). The solid was recrystallized from methanol to yield needle crystals; m.p. 235-236°C (lit.[10,69] 240°C and 233°C).

IR (KBr): 3100 (s, br), 2810 (sh), 1685 (s, br), 1498 (s), 1410 (w), 1270 (w), 1200 (w), 985 (m), 800 (s), 750 (m) cm^{-1}.

^1H NMR (DMSO-d_6, TMS): δ 2.90 (s, 3H), 10.01 (s, 2H).

^{13}C NMR (DMSO-d_6, TMS, int. ref. DMSO-d_6): δ 24.44, 155.50.

4-Methyl-1,2,4-triazoline-3,5-dione[10]

Anhydrous sodium sulfate (35.0 g), methylene chloride (350 ml), and 4-methyl urazole (5.0 g, 0.052 mole) were placed into a 500 ml three-necked round-bottomed flask which was fitted to a gas inlet tube. The slurry was stirred by a magnetic stirrer and cooled to -6°C with an ice-salt bath. Gaseous dinitrogen tetroxide was bubbled slowly through the solution over a period of 15 minutes. The temperature was kept below 0°C. After a few minutes, a deep-pink color developed. The pink solution was allowed to stir for 20 minutes more, then was filtered. The excess N_2O_4 was swept out with dry nitrogen (about 3 hours). The deep-pink solution was evaporated using lukewarm water on a rotary evaporator to yield 5.30 g (90.0%) of pink crystals; m.p. 105-106°C (lit.[10] 98-98.5°C). The product did not require further purification, and was stored in the absence of light in a desiccator until used.

Elemental analysis calculated for $C_3H_3N_3O_2$: C, 31.87; H, 2.67; N, 37.16. Found: C, 31.89; H, 2.67; N, 37.10.

IR (KBr): 3585 (w), 2960 (w), 1780 (s), 1730 (s), 1538 (w), 1600 (w), 1443 (s), 1390 (s), 1270 (s), 1100 (s), 1022 (w), 850 (s), 735 (s), 670 (s), 625 (m) cm^{-1}.

Reaction of Isoeugenol (91) With Methyl Isocyanate[71]

Synthesis of 2-Methoxy-4-propenylphenyl methylcarbamate (93)

Into a 500 ml one-necked round-bottomed flask, 10.0 g (0.0609 mole) of isoeugenol (2-methoxy-4-propenylphenol) was dissolved in 200 ml of ligroin (b.p. 20-40°C). Methyl isocyanate (6.94 g, 2 x 0.0609 mole) and 200 ml of triethylamine were added to this solution. The mixture was stirred by a magnetic stirrer and heated by means of a heating mantle to the reflux temperature for 57 hours. A white precipitate was formed. At the end of the refluxing period, the mixture was allowed to cool to room temperature, and the white solid was filtered using suction filtration, and dried, to yield 11.20 g (83.0%) of product. Recrystallization from ethylacetate/hexane gave colorless crystals; m.p. 130.5-131.0°C.

Elemental analysis calculated for $C_{12}H_{15}NO_3$: C, 65.14, N, 6.83, N, 6.33. Found: C, 65.06, H, 6.83, N, 6.31.

IR (KBr): 3320 (s), 3065 (w), 3038 (w), 3006 (m), 2960 (m), 2920 (m), 2905 (m), 2880 (m), 2820 (m), 2485 (w), 2320 (w), 2200 (w), 2065 (w), 2016 (w), 1890 (w), 1738 (s), 1714 (s), 1656 (w), 1602 (s), 1535 (s), 1500 (s), 1462 (s), 1418 (s), 1380 (m), 1331 (m), 1300 (m), 1260 (s), 1200 (s), 1155 (s), 1125 (s), 1100 (m), 1035 (s), 975 (s), 950 (m), 933 (m), 920 (m), 855 (s), 820 (w), 790 (w), 765 (w), 735 (m), 690 (m), 660 (m, br), 615 (w) cm^{-1}.

^1H NMR (DMSO-d_6, TMS): δ 1.83 (d, 3H, J = 4.6 Hz), 2.66 (d, 3H), J = 4.6 Hz), 3.75 (s, 3H), 6.31 (m, 2H), 6.90 (m, 2H), 7.04 (m, 1H), 7.51 (q, 1H, J = 4.6 Hz).

^{13}C NMR (DMSO-d_6, TMS, int. ref. DMSO-d_6): δ 18.20, 27.14, 55.53, 109.55, 117.90, 123.32, 125.46, 130.42, 135.79, 138.89, 151.71, 154.79.

LRMS (70 ev, m/e, rel. intensity): 222 (M+1, 0.2), 221 (M+, 1.1), 165 (11.2), 164 (100), 149 (23.3), 133 (9.3), 131 (11.7), 121 (9.2), 104 (9.1), 103 (13.4), 91 (15.4), 77 (17.0), 67 (10.8), 55 (16.1).

HRMS ($C_{12}H_{15}O_3N$ requires: 221.1051): Found: 221.1039.

Model Compounds Synthesis

Reaction of 2-Methoxy-4-propenylphenyl methylcarbamate (93) with 4-Methyl-1,2,4-triazoline-3,5-dione (2a) in Methylene Chloride

Into a 100 ml one-necked round-bottomed flask, 2.00 g (1.77 x 10^{-2} mole) of 4-methyl-1,2,4-triazoline-3,5-dione was dissolved in 30 ml of CH_2Cl_2. The deep-pink solution was stirred by a magnetic stirrer and cooled in an ice bath. A solution of 1.96 g (8.84 x 10^{-3} mole) of 2-methoxy-4-propenylphenyl methylcarbamate in 10 ml of CH_2Cl_2 was added all at once. The pink color changed to pale-yellow in less than 40 seconds with an exothermic reaction. The mixture was allowed to stir overnight at room temperature. A white precipitate formed, which was filtered using suction filtration. The white solid was dried in a vacuum desiccator for a few hours to yield 2.85 g of product. The mother liquor was evaporated, leaving 0.76 g of pale-yellow solid. IR and NMR of this compound are almost identical to the above solid with some impurities. The total yield was 91%. Recrystallization of the white compound from H_2O/EtOH in a ratio of 7:1 gave shiny crystals, m.p. 211-215°C.

Elemental analysis calculated for $C_{18}H_{21}N_7O_7$: C, 48.32; H, 4.73; N, 21.92. Found: C, 48.38; H, 4.74; N, 21.88.

IR (KBr) 3545 (w), 3310 (m), 3120 (m, br), 2960 (w), 2930 (w), 1775 (s), 1720 (s), 1685 (s), 1550 (w), 1510 (s), 1460 (s), 1430 (m), 1390 (m), 1360 (w), 1310 (m), 1260 (s), 1200 (w), 1160 (m), 1150 (w), 1130 (m), 1090 (w), 1050 (m), 1020 (m), 1000 (m), 965 (w), 940 (m), 910 (w), 880 (m), 850 (m), 805 (w), 760 (m), 750 (m), 720 (m), 710 (w), 676 (w), 640 (w) cm^{-1}.

LRMS (70 eV, m/e, rel intensity) 447 (M^+, 0.2), 275 (37.8), 275 (100.0), 260 (34.6), 203 (11.5), 190 (67.7), 178 (27.7), 176 (22.6), 148 (15.6), 147 (40.6), 115 (67.0), 91 (11.4), 65 (12.2), 58 (61.4), 57 (76.6), 28 (74.6).

HRMS ($C_{18}H_{21}O_7N_7$ requires 447.1502). Found 447.1499.

Reaction of 2-Methoxy-4-propenylphenyl Methylcarbamate (§3) with 4-Phenyl-1,2,4-triazoline-3,5-dione (2b) in Methylene Chloride

A 100 ml round-bottomed flask was charged with 1.58 g (9.04 x 10^{-3} mole) of 4-phenyltriazolinedione and 40 ml of methylene chloride. The red solution was cooled in an ice bath with stirring. To this red solution, a solution of 1.00 g (4.52 x 10^{-3} mole) of 2-methoxy-4-propenylphenyl methylcarbamate in 10 ml of methylene chloride was added all at once. An exothermic reaction occurred, and the characteristic red color of PhTD disappeared in less than 40 seconds. After about 3 minutes, a white precipitate began to form, and the mixture was stirred at room temperature for 24 hours. The white solid was filtered using suction filtration, then was dried in a vacuum desiccator for several hours to yield 2.20 g of product. The yellowish mother liquor was evaporated to dryness to give 0.19 g of pale-yellow solid. The total yield was 93%. Recrystallization of the

white solid from 95% ethanol led to a crystalline solid, m.p. 188-191°C.

Elemental analysis calculated for $C_{28}H_{25}N_7O_7$: C, 58.84; H, 4.41; N, 17.16. Found: C, 58.69; H, 4.38; N, 17.07.

IR (KBr): 3360 (m), 3220 (w), 3150 (w), 3080 (w), 2960 (w), 2740 (w), 1760 (s), 1715 (s), 1700 (s), 1620 (w), 1600 (w), 1500 (s), 1420 (s), 1318 (m), 1270 (m), 1240 (m, br), 1190 (m), 1130 (m), 1095 (w), 1045 (m), 1020 (m), 960 (w), 915 (m), 880 (m), 800 (w), 760 (m), 725 (w), 690 (m), 648 (w), 625 (w) cm^{-1}.

LRMS (70 eV/ m/e, rel. intensity): 338 (13.0), 337 (58.6), 190 (100.0), 177 (72.1), 147 (38.0), 120 (35.6), 119 (79.5), 91 (37.2), 77 (44.2), 57 (93.0), 56 (34.7), 39 (18.8).

HRMS (M-$C_{10}H_{10}N_4O_3$ = $C_{18}H_{15}N_3O_4$ requires 337.1062): Found: 337.1052.

Synthesis and Identification of Bis-triazolinediones

Synthesis of 1,6-Bis-(3,5-dioxo-1,2,4-triazoline-4-yl) hexene (108)[72]

1,6-Hexane-bis-semicarbazide (102)

1,6-Hexene diisocyanate was obtained from Eastman Chemical Co., and was used without further purification.

To a 500 ml three-necked round-bottomed flask equipped with a water-cooled condenser attached to a drying tube containing silica gel, a mechanical stirrer, an addition funnel and a thermometer was added 46.5 g (0.476 mole) of ethylcarbazate and 200 ml of dry benzene. The solution was stirred and cooled in an ice bath at approximately 10°C. A solution of 40.03 g (0.238 mole) of 1,6-hexane diisocyanate in 10 ml of benzene was added dropwise over a period of 40 minutes

The temperature was kept at approximately 20-30°C. After 2 minutes, a white solid began to form, and a thick solid was obtained by the end of the addition. The voluminous white slurry was stirred at room temperature for 45 minutes, then was refluxed for 2 hours. The mixture was cooled, and the white solid was filtered using suction filtration, then dried overnight in a vacuum oven at 50°C to yield 88-94 g (99-3%) of white solid, m.p. 202-203°C.

IR (KBr) 3330 (s), 3240 (s), 3120 (s), 2960 (s), 2940 (s), 2860 (m), 1705 (s), 1640 (s), 1565 (s), 1500 (m), 1480 (m), 1420 (m), 1380 (m), 1335 (s), 1290 (w), 1230 (m), 1180 (m), 1135 (w), 1100 (w), 1070 (s), 960 (w), 925 (w), 865 (w), 800 (w), 755 (m), 730 (w), 690 (w) cm^{-1}.

^1H NMR (DMSO-d_6, TMS) δ 1.17 (distorted t, 14H, CH_2 peaks are overlapped with CH_3 peaks, J = 7.2 Hz), 2.96 (m, 4H), 3.37 (s, 1H perhaps due to tautomerization), 4.02 (q, 4H, J = 7.2 Hz), 6.31 (distorted t, 2H), 7.62 (s, 2H), 8.70 (s, 2H).

^{13}C NMR (DMSO-d_6, TMS, int. ref. DMSO-d_6) δ 14.54, 26.05, 29.85, 39.11, 60.36, 155.91, 158.27.

1,6-Hexane-bis urazole (106)

Sodium metal[73] (4.90 g, 0.212 mole) was placed in a 1000 ml three-necked round-bottomed flask which was flushed with dry nitrogen gas. The flask was equipped with a mechanical stirrer, an addition funnel, and a reflux condenser fitted with a drying tube containing calcium chloride. Absolute ethanol (490 ml) was added dropwise over a period of 45 minutes. The solution began to reflux, and at the end of the addition a clear solution was obtained. This solution was

heated by means of a heating mantle to the reflux point, and 40.0 g (0.106 mole) of 1,6-hexane bis-semicarbazide was added all at once. An orange solution was obtained, which then turned to red. After a few minutes, a precipitate started to form, and the color changed from red to orange. The slurry mixture was refluxed for 36 hours. The light-yellow solid was collected with suction filtration, and then dried in a vacuum oven at 50°C for 24 hours to yield 34.80 g (100%) of disodium salt; m.p. >300°C.

IR (KBr): 3200 (s, br), 3080 (w), 2950 (w), 2920 (w), 2860 (w), 1695 (s), 1600 (s, br), 1470 (s), 1430 (w), 1380 (m), 1280 (w), 1220 (w), 1080 (m), 820 (s), 810 (s), 765 (m), 735 (w), 690 (w), 670 (w), 640 (m) cm^{-1}.

The pale-yellow disodium salt (10.0 g, 0.030 mole) was placed in a 100 ml beaker, and 20 ml of 95% ethanol was added. The mixture was stirred by means of a magnetic stirrer and acidified with glacial acetic acid (about 11 ml is required). A clear yellowish solution was obtained, 40 ml of methylene chloride was added, and the mixture was kept in a freezer for 8 hours. The white solid that formed was filtered and washed with 200 ml of cooled water. The solid was dried overnight in a vacuum oven at 100°C to yield 6.50 g (76%) of bis urazole. Recrystallization from hot water furnished white crystals, m.p. 223-224°C.

Elemental analysis calculated for $C_{10}H_{16}N_8O_4$: C, 42.25; H, 5.67; N, 29.56. Found: C, 42.28; H, 5.67; N, 29.60.

IR (KBr): 3300 (s), 3180 (s, br), 2940 (m), 2920 (m), 2820 (w), 1695 (s, br), 1540 (w), 1475 (s), 1430 (m), 1375 (w), 1360 (w), 1325

(m), 1260 (w), 1210 (w), 1188 (w), 1080 (m), 975 (m), 950 (m), 790 (s, br), 725 (w), 680 (w), 630 (w), 605 (w) cm^{-1}.

^1H NMR (DMSO-d_6, TMS): δ 1.40 (m, 9H), 3.36 (t, 4H, J = 6.4 Hz), 9.77 (s, br, 4H).

^{13}C NMR (DMSO-d_6, TMS, int. ref. DMSO-d_6): δ 25.76, 27.56, 37.94, 155.26.

1,6-bis-(3,5-dioxo-1,2,4-triazolidin-4-yl)hexane (10e)

A 250 ml one-necked round-bottomed flask was charged with 2.85 g (0.010 mole) of 1,6-hexane-bis urazole (10b) and 160 ml of methylene chloride. The suspension was stirred with a magnetic stirrer and cooled in an ice-salt bath to -10°C. Fuming nitric acid (3.0 ml, 0.071 mole) was added dropwise over a period of 30 minutes. The solution turned to a deep-pink color and was filtered using gravity filtration into a 500 ml separatory funnel. The deep-pink solution was washed with ice-water (4 x 100 ml), then was dried overnight over anhydrous sodium sulfate in a freezer. The pink solution was filtered, and the methylene chloride was evaporated at room temperature, leaving 2.25 g (80.3%) of a light-pink solid. Purification was performed by dissolving the pink solid in 10 ml of ethyl acetate and filtering, then slowly dropping into 100 ml of cyclohexane, resulting in precipitation of a pink solid, m.p. 146.0-149.0°C.

Elemental analysis calculated for $C_{10}H_{12}N_6O_4$: C, 42.86; H, 4.32; N, 29.99. Found: C, 42.92, H, 4.34, N, 29.91.

IR (KBr): 3580 (w), 2950 (m), 2920 (m), 2860 (w), 1755 (s), 1625 (w), 1459 (w), 1446 (w), 1445 (m), 1395 (s), 1355 (m), 1330 (m), 1255 (m), 1190 (m), 1130 (m), 1040 (m), 960 (m), 950 (w), 950 (m), 729 (s), 675 (s), 612 (w) cm^{-1}.

Synthesis of 9is-(p-3,5-dioxo-1,2,4-triazoline-4-ylphenyl)methane[51,73] (103)

4,4'-Diphenylmethane-bis-semicarbazine (103)

4,4'-Diphenylmethane (100) was purchased from Eastman Chemical Co and was purified via vacuum distillation at 137°C and a pressure of 0 12 mm Hg

Into a 500 ml three-necked round-bottomed flask was placed 13 83 g (0.190 mole) of ethyl carbazate and 150 ml of dry benzene The flask was equipped with a thermometer, a mechanical stirrer, a water-cooled condenser fitted to a drying tube containing silica gel, and a constant pressure funnel The stirrer was started, and a solution of 23 83 g (0.095 mole) of 4,4'-diphenylmethane diisocyanate in 130 ml of dry benzene was added dropwise at room temperature over a period of 3 hours. The temperature was kept at 40-45°C After the addition was complete, the voluminous white slurry was gently refluxed for 3 hours At the end of refluxing, the mixture was cooled, filtered, and then washed with 400 ml of diethyl ether and dried overnight in a vacuum oven at 85°C to yield 40.30 g (93.7%) of a white solid, m.p 253.0-256.0°C [lit[74] 240.0-242.0°C (dec)]

IR (KBr) 3360 (s, br), 3295 (s, br), 3030 (w), 2980 (w), 2940 (w), 2920 (w), 1735 (s), 1680 (s), 1645 (s), 1600 (s), 1555 (s), 1510 (s), 1412 (w), 1315 (s), 1230 (s), 1110 (w), 1090 (w), 1058 (m), 1035 (m), 910 (w), 850 (w), 820 (w), 770 (m), 620 (m) cm^{-1}

^{1}H NMR (DMSO-d_6, TMS) δ 1.18 (t, 6H, J = 7.0 Hz), 3.79 (s, 2H), 4.05 (q, 4H, J = 7.0 Hz), 7.38 (d, 4H, AA', J = 8.4 Hz), 7.07 (d, 4H, XX', J = 8.4 Hz), 7.96 (s, 2H), 8.65 (s, 2H), 8.96 (s, 2H)

4,4'-(4,4'-Diphenylmethylene)-bis urazole (107)

Into a 250 ml beaker was placed 16.86 g (0.037 mole) of 4,4'-diphenylmethane-bis-semicarbazide (103) and 50 ml of absolute ethanol. To this mixture, 60 ml of 4N potassium hydroxide was added all at once. The mixture was stirred by a magnetic stirrer at room temperature. After about 10 minutes, a pale-yellow solution was obtained which was warmed on a water bath for 2 hours. The solution was filtered, cooled in an ice bath and then acidified with 20 ml of concentrated hydrochloric acid. A white solid formed, which was filtered using suction filtration and washed twice with 25 ml of H_2O, followed by 25 ml of ethanol. This white solid was dried in an oven under vacuum at 75°C for 24 hours to give 11.10 g (82.4%) of product. Recrystallization was performed from hot methanol H_2O (2:1) to afford white crystals, m.p. >300°C.

IR (KBr): 3400 (w), 3140 (s, br), 2920 (w), 1765 (sh), 1700 (s), 1680 (s), 1510 (s), 1445 (s), 1210 (w), 1120 (w), 1090 (w), 1030 (w), 1010 (w), 870 (w), 840 (w), 785 (s), 760 (w), 715 (w), 650 (w).

^{1}H NMR (DMSO-d_6, TMS): δ 4.00 (s, 2H), 7.39 (m, 8H), 10.43 (s, br, 4H).

^{13}C NMR (DMSO-d_6, TMS, int. ref. DMSO-d_6): δ 40.11, 125.97, 128.96, 129.84, 140.46.

Bis-(p-3,5-dioxo-1,2,4-triazoline-4-ylphenyl)methane (109)

Two methods were employed for the preparation of this compound:

Method A. 4,4'(4,4'-Diphenylmethylene)-bis urazole (107) (3.0 g, 8.19 x 10^{-3} mole) and 400 ml of methylene chloride were placed into a 500 ml three-necked round-bottomed flask. To this mixture, 30.0 g of

anhydrous sodium sulfate was added, and the suspension was stirred by a magnetic stirrer. The flask was fitted with a gas inlet tube and cooled in an ice-salt bath to -6°C. Gaseous dinitrogen tetroxide was bubbled through the solution for 20 minutes, while the temperature was kept below 0°C. A deep-red solution was obtained, which was stirred at room temperature for 30 minutes, then filtered using gravity filtration. The excess N_2O_4 was purged with dry nitrogen for 2 hours. The solvent was evaporated by rotary evaporation. A red solid which resulted was dried under vacuum overnight at room temperature to yield 2.48 g (83.5%). Further purification was achieved by dissolving 1.48 g of the red solid in 40 ml of ethyl acetate and adding the solution dropwise to 450 ml of n-hexane, leaving a red precipitate, m.p. >185°C (dec).

Method B. 4,4'(4,4'-Diphenylmethylene)-bis urazole (107) (2.00 g, 0.00546 mole) which was suspended in 150 ml of CH_2Cl_2 was placed into a 250 ml one-necked round-bottomed flask. The mixture was cooled in an ice-salt bath to -10°C. Fuming nitric acid (1.1 ml) was added dropwise over a period of 5 minutes. A deep-red solution was obtained which was stirred at -10°C for 30 minutes. The red solution was filtered, washed with 250 ml of ice-water in a separatory funnel, and dried over anhydrous sodium sulfate (25.0 g) in a freezer for 24 hours. The solvent was removed by rotary evaporation, resulting in 1.0 g of red solid (50.5%). Purification was performed as in Method A.

IR (KBr). 3590 (w), 3050 (w), 1900 (w), 1845 (w), 1768 (s), 1710 (sh), 1640 (w), 1600 (w), 1510 (s), 1435 (m), 1395 (s), 1300 (w),

1176 (s), 1156 (m), 1020 (m), 960 (w), 900 (m), 850 (w), 813 (m), 790 (w), 740 (s), 720 (w), 685 (s), 635 (w), 625 (w) cm^{-1}.

Copolymerization Reactions

Reaction of 2-Methoxy-4-propenylphenyl Methylcarbamate (93) with 1,6-bis-(3,5-dioxo-1,2,4-triazoline-4-yl)hexane (108) in DMF

Into a 500 ml round-bottomed flask equipped with a magnetic stirrer bar was placed 1.60 g (5.35×10^{-3} mole) of 1,6-bis-(3,5-dioxo-1,2,4-triazoline-4-yl)hexane (108) and 10 ml of N,N-dimethylformamide (DMF). The red solution was stirred with a magnetic stirrer at room temperature, and a solution of 1.18 g (5.35×10^{-3} mole) of 2-methoxy-4-propenylphenyl methylcarbamate (93) in 5 ml of DMF was rapidly added all at once. The red solution turned to a pale-yellow color in less than 40 seconds with an exothermic reaction. The mixture was stirred at room temperature for 48 hours. The pale-yellow solution was filtered through glass wool and added dropwise to 400 ml of diethyl ether, resulting in a white precipitate, which was filtered using suction filtration and dried in a vacuum oven at 90°C for 48 hours to yield 2.40 g (90.0%) of product. Further purification was performed by dissolving the white solid in 20 ml of DMF and precipitation into 400 ml of diethyl ether. This procedure was repeated twice; m.p. >215°C (dec).

Elemental analysis calculated for $C_{22}H_{27}N_7O_7$ (1:1): C, 52.68; H, 5.43; N, 19.56. Found: C, 51.39; H, 5.57; N, 19.06.

IR (KBr): 3360 (m, br), 2940 (m), 2860 (w), 1760 (s), 1700 (s, br), 1505 (s), 1458 (s), 1420 (s), 1360 (w, br), 1310 (w), 1240 (m), 1180 (w), 1059 (w), 1005 (w), 930 (w), 890 (w), 760 (m, br), 725 (w) cm^{-1}.

Intrinsic viscosity (N,N-dimethyl formamide, 30.0°C): [η] = 0.205 dl/g;

$\bar{M}_n$ = 13000 (MO, N,N-dimethyl formamide, 38.0°C, membrane RC-51 S & S).

Reaction of 2-Methoxy-4-propenylphenyl Methylcarbamate (93) with Bis-(p-3,5-dioxo-1,2,4-triazoline-4-ylphenyl)methane (109)

Bis-(p-3,5-dioxo-1,2,4-triazoline-4-ylphenyl)methane (109) (0.898 g, 2.48 x 10^{-3} mole) and 7.5 ml of N,N-dimethyl formamide were placed into a 50 ml round-bottomed flask. The mixture was stirred, and a red solution was obtained. To this solution, 0.548 g (2.48 x 10^{-3} mole) of 2-methoxy-4-propenylphenyl methylcarbamate in 5 ml of N,N-dimethyl formamide was added all at once. An exothermic reaction was observed, and the red color disappeared in less than 35 seconds. The pale-yellow solution was stirred at room temperature for 48 hours, then was added to 300 ml of diethyl ether. The precipitated solid was filtered and dried in a vacuum oven at 100°C for 48 hours, affording 1.40 g (97.2%) of off-white material. Further purification was accomplished by dissolving the solid in 13 ml of DMF and precipitation into 300 ml of diethyl ether, m.p. >235 (dec).

Elemental analysis calculated for $C_{29}H_{25}N_7O_7$ (1:1): C, 59.68; H, 4.32; N, 16.80. Found: C, 57.07; H, 4.50; N, 15.74.

IR (KBr): 3400 (m, br), 2940 (w), 1765 (sh), 1710 (s, br), 1510 (s), 1420 (s, br), 1315 (w), 1270 (m), 1240 (w), 1190 (w), 1130 (w), 1100 (w), 1045 (w), 1020 (m), 910 (w), 820 (w), 750 (w, br) cm^{-1}.

Intrinsic viscosity (N,N-dimethyl formamide, 30.0°C) [η] = 0.205 dl/g.

Synthesis of S-(-)-4-(α-Methylbenzyl)-1,2,4-triazoline-3,5-dione, S-(-)CTD (119)

S-(-)-α-Methylbenzylamine Hydrochloride (115)

Into a 1000 ml, three-necked round-bottomed flask equipped with a gas-inlet tube and a mechanical stirrer (all glassware was flame-dried prior to use) was charged 26.19 g (0.2161 mole) of S-(-)-α-methylbenzylamine ($[\alpha]_0^{20}$ -30 ± 2°, C = 10 in ethanol) and 700 ml of dry toluene. The mixture was cooled in an ice-water bath, and dry hydrogen chloride gas was passed through the solution for 15 minutes. A white crystalline solid was formed. The HCl flow was discontinued, and the ice-water bath was removed. Dry nitrogen gas was passed through the slurry mixture for 1 hour, and the excess HCl was trapped with a 20% NaOH solution. After the white solid was filtered using suction filtration, washed with 500 ml of anhydrous diethylether, and dried overnight in a vacuum desiccator, 33.45 g (98.2%) of a white crystalline solid was obtained; m.p. 169.0 ~ 170.0°C.

IR (KBr): 2920 (s, br), 2725 (sh), 2675 (sh), 2630 (sh), 2570 (sh), 2480 (m), 2030 (m), 1600 (m), 1505 (s), 1450 (s), 1380 (m), 1357 (w), 1332 (w), 1312 (w), 1289 (w), 1225 (m), 1087 (m), 1064 (m), 1028 (w), 986 (w), 920 (w), 758 (s), 746 (m), 694 (s) cm^{-1}.

^1H NMR (DMSO-d_6, TMS): δ 1.55 (d, 2H, J = 7.0 Hz), 4.38 (q, 1H, J = 7.0 Hz), 7.5 (m, 5H), 8.83 (s, br, 3H) which exchanges with D_2O.

^{13}C NMR (DMSO-d_6, TMS, int. ref. DMSO-d_6): 20.88, 50.08, 126.89, 128.20, 128.64, 139.51.

$[\alpha]_0^{25}$ -19.8 (C = 10.0, CH_2Cl_2).

S-(-)-α-Methylbenzyl Isocyanate (116)

Into a 1000 ml three-necked round-bottomed flask equipped with a mechanical stirrer, water cooled condenser and gas inlet tube was placed 29.05 g (0.1843 mole) of S-(-)-α-methylbenzylamine hydrochloride (115) and 600 ml of dry toluene. The slurry mixture was heated to reflux temperature. Phosgene gas was bubbled into the mixture until all solid had completely dissolved (~3 hour), then again for an additional hour. The phosgene gas was routinely passed through two traps and towers containing cottonseed oil, concentrated sulfuric acid and $CaSO_4$ prior to passing into the reaction vessel. The HCl gas generated from the reaction and excess $COCl_2$ gas were trapped in a 20% NaOH solution. The hot, clear solution was flushed with dry nitrogen gas for 1 hour. Toluene was removed via simple distillation at atmospheric pressure, and the residue was distilled under vacuum to yield 23.3 g of a clear liquid (85.9%), b.p. 104-106°C/30 mm Hg.

Elemental analysis calculated for C_9H_9NO: C, 73.45; H, 6.16; N, 9.62. Found: C, 73.55; H, 6.20; N, 9.49.

IR (neat): 3060 (m), 3047 (m), 3032 (m), 3008 (m), 2980 (m), 2936 (m), 2260 (s), 1950 (w), 1880 (w), 1820 (w), 1750 (w), 1620 (w), 1605 (m), 1495 (m), 1452 (m), 1372 (m), 1348 (m), 1310 (m), 1280 (m), 1205 (m), 1064 (m), 1028 (m), 910 (m), 830 (m), 750 (m), 697 (s) cm^{-1}.

^1H NMR ($CDCl_3$, TMS): δ 1.59 (d, 3H, J = 6.8 Hz), 4.8 (q, 1H, J = 6.8 Hz), 7.3 (s, 5H).

^{13}C NMR ($CDCl_3$, TMS, int. ref. $CDCl_3$): 25.97, 54.68, 125.30, 127.78, 128.71, 142.40 (C = O carbon is overlapped with aromatic carbons).

$[\alpha]_D^{25}$ -13.9° (C = 10.05, CH_2Cl_2), Lit [75] $[\alpha]_D^{20.5}$ -10.1°.

LRMS (70 eV, m/e, rel intensity): 148 (M + 1, 3.8), 147 (M^+, 36.8), 132 (100.0), 105 (23.5), 78 (18.3), 77 (38.5), 51 (18.5), 39 (4.8), 27 (4.5).

HRMS (C_8H_9HO requires: 147.0684) Found 147.0676.

S-(-)-4-(α-Methylbenzyl)-1-(ethoxycarbonyl)semicarbazide (117)

Into a 250 ml three-necked flask fitted with a constant-pressure dropping funnel, magnetic bar, reflux condenser attached to a drying tube containing silica gel, and a thermometer was placed a solution of 16.27 g (0.1563 mol) of ethylhydrazine carboxylete[6,69] in 60 ml of dry toluene. A solution of 23.00 g (0.1563 mole) of S-(-)-α-methylbanzylisocyanate (116) in 60 ml of dry toluene was added dropwise to this mixture over a period of 1½ hour. The temperature was kept below 40°C. After addition was complete, the mixture was heated at reflux temperature for 8 hour (2 hour will be enough). The mixture was cooled and stirred at room temperature for 60 hour to effect crystallization. (Solidification also can occur in a shorter period of time, ~4 hour, if a few previously formed crystals are added.) The white solid was filtered using suction filtration, washed with 500 ml of petroleum ether (b.p. 37-38°C), then dried in a vacuum desiccator for 24 hour to give 38.21 g of a white solid (97.3%), m.p. 87.0 - 89.0°C.

Elemental analysis calculated for $C_{12}H_{17}N_3O_3$: C, 57.35, H, 6.82, N, 16.73. Found: C, 57.80, H, 6.85, N, 16.75.

IR (KBr): 3360 (s), 3280 (s), 3110 (w), 3060 (w), 3037 (w), 2980 (m), 2940 (w), 2810 (w), 2870 (w), 1700 (s), 1650 (s), 1600 (w), 1545 (s), 1480 (w), 1475 (w), 1450 (w), 1379 (m), 1349 (m), 1335 (m), 1320

(m), 1280 (m), 1228 (m), 1140 (m), 1070 (s), 1028 (w), 1000 (w), 990 (w), 915 (w), 780 (w), 758 (m), 695 (s), 660 (w) cm^{-1}.

^1H NMR (DMSO-d_6, TMS) δ 1.16 (t, 3H, J = 7.0 Hz), 1.35 (d, 3H, J = 7.0 Hz), 4.03 (q, 2H, J = 7.0 Hz), 4.30 (P, 1H, J = 7.0 Hz), 6.73 (d, 1H, J = 8.0 Hz), 7.29 (m, 5H), 7.67 (s, 1H), 8.78 (s, br, 1H).

^{13}C NMR (DMSO-d_6, TMS, int. ref. DMSO-d_6) 14.50, 22.88, 48.57, 60.36, 125.86, 126.45, 128.10, 145.31, 156.96, 157.45.

$[\alpha]_D^{25}$ -3.7 (C = 10.0, CH_2Cl_2).

LRMS (70 eV, m/e, rel. intensity): 147 (3.2), 132 (15.9), 120 (5.9), 105 (100.0), 104 (64.6), 79 (17.5), 77 (36.8), 51 (17.2), 45 (15.4), 42 (11.1), 32 (17.6), 29 (24.0), 27 (17.3).

S-(-)-4-(α-Methylbenzyl)urazole (118)

Into a 250 ml round-bottomed flask equipped with a magnetic stirring bar, distillation head, thermometer and a water-cooled condenser was placed 40.31 g (0.1604 mole) of 5-(-)-4-(α-methylbenzyl)-1-(ethoxycarbanyl)semicarbazide (117). The flask was heated to 250-260°C using a sand bath for 1½ hour. The distillate, which was collected between 80-95°C, was discarded. The residue was cooled, 200 ml of benzene was added, and the mixture was heated to the boiling point of the solvent. The hot mixture was filtered and cooled to give 24.60 g (74.7%) of a white solid. Recrystallization from benzene yielded a white crystalline solid, m.p. 126.0-127.5°C.

Elemental analysis calculated for $C_{10}H_{11}H_3O_2$: C, 58.52; H, 6.40; N, 20.48. Found: C, 58.67; H, 5.44; N, 20.42.

IR (KBr): 3160 (sh), 3030 (s), 2972 (s), 2800 (s, br), 1760 (sh), 1675 (s), 1490 (m), 1450 (s), 1375 (m), 1310 (w), 1280 (w), 1238 (m),

1217 (m), 1207 (m), 1160 (w), 1140 (w), 1110 (w), 1080 (m), 1055 (m), 1025 (m), 1003 (w), 980 (w), 919 (w), 775 (s), 695 (s), 665 (w), 623 (w) cm^{-1}

^1H NMR (DMSO-d_6, TMS) δ 1.76 (d, 3H, J = 7.4 Hz), 5.17 (q, 1H, J = 7.4 Hz), 7.33 (m, 5H), 9.97 (s, br, 2H).

^{13}C NMR (DMSO-d_6, TMS, int. ref. DMSO-d_6) 17.37, 49.34, 126.69, 127.37, 128.40, 140.92, 154.71

$[\alpha]_D^{25}$ -43.4 (C = 10.0, CH_2Cl_2).

LRMS (70 eV/ m/e, rel. intensity) 206 (M + 1, 1.3), 205 (M^+, 10.0), 106 (10.0), 105 (100.0), 77 (19.1), 51 (10.0), 39 (3.7), 28 (6.2).

HRMS ($C_{10}H_{11}N_3O_2$ requires 205.6851) Found 205.6842

S-(-)-4-(α-Methylbenzyl)-1,2,4-triazaline-3,5-dione (119)

Anhydrous sodium sulfate (40.0 g) was placed into a 300 ml round-bottomed flask with 6.00 g (0.0292 mole) of S-(-)-4-(α-methylbenzyl)-urazole (118) and 160 ml of methylene chloride. The slurry mixture was stirred by a magnetic stirrer and cooled to -5°C with an ice-salt bath. Dinitrogen tetraoxide gas was bubbled slowly through the mixture for 10 minutes, while keeping the temperature below 0°C. After a few minutes, a deep-red color developed. The red solution was stirred for 30 minutes, then filtered into a 250 ml round-bottomed flask. The excess N_2O_4 was flushed with dry nitrogen gas (~3 hour), and the solvent was removed by rotoevaporation to give a deep-pink viscous liquid. Upon scratching the interior part of the flask, a dark-pink crystalline solid was formed. The pink crystals were dried

overnight under vacuum at room temperature to give 5.67 g (95.6%) of pink crystals; m.p. 74-78°C. Sublimation was accomplished at 60-70°C under a vacuum of less than 0.6 mm; m.p. 78-81°C, lit.[76] m.p. 57-61°C. The pink solid was stored in the absence of light in a desiccator until it was used.

IR (KBr) 3580 (w), 3090 (w), 3070 (w), 2990 (m), 2942 (w), 2878 (w), 1985 (w), 1960 (w), 1915 (w), 1760 (s), 1665 (sh), 1588 (w), 1520 (w), 1495 (m), 1460 (m), 1385 (s), 1375 (s), 1345 (s), 1285 (m), 1215 (m), 1180 (s), 1160 (m), 1115 (w), 1080 (w), 1060 (w), 1020 (m), 980 (m), 935 (m), 840 (w), 780 (s), 770 (m), 735 (s), 700 (s), 680 (s), 650 (w), 640 (m) cm^{-1}.

^1H NMR (DMSO-d_6, TMS) δ 1.76 (d, 3H, J = 7.2 Hz), 5.25 (q, 1H, J = 7.3 Hz), 7.40 (m, 5H).

^{13}C NMR (DMSO-d_6, TMS, int. ref. DMSO-d_6) 17.13, 62.66, 126.93, 128.01, 128.45, 138.44, 159.69.

$[\alpha]_D^{25}$ -61 (C = 2.0, CH_2Cl_2) Lit.[76] $[\alpha]_D^{25}$ -48.6 (C = 3.7, CH_2Cl_2).

Synthesis of Model Compounds

5-(-)-4-(α-Methylbenzyl)-1-allylurazole (121)

5-(-)-4-(α-Methylbenzyl)-1,3,5-triazolline-2,4-dione (119) (1.5 g, 0.0073 mole) was placed in a 50 ml round-bottomed flask with 15 ml of methylene chloride. The dark-pink solution was stirred by a magnetic stirrer, and propylene was bubbled slowly through the solution until all the pink color had disappeared (~4 hour). Methylene chloride was removed by rotoevaporation, and a pale-yellow viscous oil remained. Ether was added (5 ml), and slow evaporation gave 1.81 g of a white solid (100%). Purification was performed by sublimation at 80°C under a vacuum of less than 0.3 mm, m.p. 73.5-76.0°C.

Elemental analysis calculated for $C_{13}H_{15}N_3O_2$ C, 63.66; H, 6.16; N, 17.13; Found: C, 63.75; H, 6.17; N, 17.09

IR (KBr): 3450 (w), 3170 (s, br), 3017 (w), 2990 (w), 2940 (w), 2910 (w), 1770 (s), 1685 (s), 1600 (sh), 1580 (w), 1490 (m), 1440 (s), 1414 (s), 1380 (s), 1345 (m), 1305 (m), 1235 (m), 1190 (w), 1160 (w), 1110 (w), 1090 (w), 1045 (m), 1025 (m), 1000 (m), 980 (m), 930 (s), 895 (m), 845 (w), 780 (s), 760 (s), 712 (s), 695 (s), 620 (m), 610 (m) cm^{-1}.

^1H NMR (DMSO-d_6, TMS): δ 1.77 (d, 3H, J = 7.5 Hz), 4.03 (d, 3H, J = 6.0 Hz), 5.12 (m, 3H), 5.79 (tt, 1H, J = 6.0 Hz), 7.30 (m, 5H), 10.49 (s, 1H).

^{13}C NMR (DMSO-d_6, TMS, int. ref. DMSO-d_6): 17.3, 48.4, 49.8, 119.0, 126.5, 128.3, 127.4, 131.5, 140.6, 153.6, 153.4.

LRMS (70 eV, m/e, rel. intensity): 246 (M^+ + 1, 1.1), 245 (M^+, 6.5), 141 (12.9), 132 (3.9), 105 (100.0), 104 (22.8), 79 (7.2), 77 (11.8), 39 (4.4), 28 (14.5)

HRMS ($C_{13}H_{15}N_3O_2$ requires: 245.1164) Found: 245.1157

$[\alpha]_D^{25}$ -34.8 (C = 10.0, CH_2Cl_2).

S-(-)-4-(α-Methylbenzyl)-1-(2,3-dibromopropyl)urazole (125)

Into a 25 ml three-necked, round-bottomed flask, which had been wrapped with foil and equipped with a drying tube containing anhydrous $CaSO_4$ and an addition funnel, was placed 0.30 g (0.0012 mole) of S-(-)-4-(α-methylbenzyl)-1-allylurazole (121) and 7 ml of carbon tetrachloride. A solution of 0.19 g (0.0012 mole) of bromine in 5 ml of CCl_4 was added dropwise to the stirred mixture. At the end of addition, the mixture was stirred at room temperature for 2 hour

The pale-yellow solid was filtered, washed with cold CCl_4, and dried under vacuum to give 0.40 g (82%) of product. Recrystallization twice from methanol gave colorless crystals, m.p. 178.0-179.0°C.

Elemental analysis calculated for $C_{13}H_{15}N_3O_2Br_2$: C, 38.54; H, 3.73; N, 10.37. Found: C, 37.59; H, 3.57; N, 10.16.

IR (KBr): 3140 (s, br), 2992 (w), 2940 (w), 1765 (s), 1680 (s), 1495 (w), 1470 (s), 1450 (s), 1435 (s), 1388 (m), 1380 (m), 1370 (m), 1338 (w), 1280 (w), 1252 (m), 1232 (m), 1218 (m), 1200 (w), 1150 (m), 1080 (m), 1070 (w), 1050 (w), 1030 (w), 1010 (w), 1005 (w), 950 (w), 930 (m), 800 (m), 790 (m), 760 (s), 725 (m), 700 (s), 688 (m), 648 (m) cm^{-1}.

^1H NMR (DMSO-d_6, TMS): δ 1.76 (d, 3H, J = 7.5 Hz), 3.84 (dd, 2H, J = 4.5 Hz), 4.00 (m, 2H), 4.62 (m, 1H), 5.20 (q, 1H, J = 7.5), 7.31 (m, 5H), 10.52 (s, 1H).

^{13}C NMR (DMSO-d_6, TMS, int. ref. DMSO-d_6): 17.20, 35.47, 49.46, 49.73, 50.62, 126.48, 127.32, 128.25, 140.30, 153.40, 153.53.

LRMS (70 eV, m/e, rel. intensity): 323 (M^+-Br, 0.7), 245 (1.7), 141 (3.6), 105 (100.0), 104 (15.2), 82 (3.8), 80 (3.5), 77 (10.9), 51 (4.0), 41 (5.5), 39 (4.5), 28 (8.0).

HRMS ($C_{13}H_{14}O_2N_3Br$, M^+-Br requires 323.0269). Found: 323.0267.

$[\alpha]_D^{25}$ -23.0 (C = 9.90 DMSO).

Reaction of S-(-)-4-(α-Methylbenzyl)-1,2,4-triazoline-3,5-dione (113) with a Large Excess of 1,5-Hexadiene in CH_2Cl_2

A 100 ml three-necked round-bottomed flask was charged with 12.13 g (0.147 mole) of 1,5-hexadiene and 30 ml methylene chloride. The flask was equipped with a drying tube containing anhydrous Ca_2SO_4 and

a magnetic bar. The stirrer was started, and a solution of 1.00 g (0.00492 mole) of 5-(-)-4-(α-methylbenzyl)-1,2,4-triazoline-3,5-dione in 20 ml of methyl chloride was added dropwise through an addition funnel. After about 6 hours, a pale-yellow solution was obtained. The solution was stirred at room temperature overnight. Evaporation of solvent by rotary evaporation left a viscous oil, which was dried overnight in a vacuum desiccator. The yield was 1.35 g of pale-yellow oil (96.4%). Purification was performed via column chromatography using silica gel and acetone:methanol (50:50). The pure product was a pale-yellow oil.

IR (KBr): 3440 (m, br), 3170 (s, br), 3060 (m), 3020 (m), 2970 (m), 2930 (m), 1760 (s), 1690 (s), 1600 (w), 1580 (w), 1440 (m), 1425 (s, br), 1375 (m), 1220 (m, br), 1150 (w), 1080 (w), 1020 (m), 970 (m), 910 (m), 760 (s), 690 (s) cm^{-1}.

^1H NMR (DMSO-d_6, int. ref. DMSO-d_6): δ 1.74 (d, 3H, J = 7.3 Hz), 2.75 (t, 2H, J = 6.0 Hz), 3.97 (d, 2H, J = 5.5 Hz), 5.12 (m, 3H), 5.72 (m, 3H), 7.32 (m, 5H), 10.41 (s, 1H).

^{13}C NMR (DMSO-d_6, TMS, int. ref. DMSO-d_6): 17.32, 35.58, 47.67, 49.66, 115.70, 123.72, 126.41, 127.31, 128.31, 132.91, 136.05, 140.60, 153.35, 153.67.

LRMS (70 eV, m/e, rel. intensity): 285 (M^+, 1.03), 205 (6.71), 105 (100.00), 81 (28.26), 77 (11.16), 67 (3.23), 57 (1.82), 53 (4.45), 51 (3.33), 41 (6.61), 28 (6.44).

HRMS ($C_{16}H_{19}N_3O_2$ requires 285.1477). Found: 285.1475.

$[\alpha]_D^{25}$ -25.8 (C = 16.76, CH_2Cl_2).

Reaction of S-(-)-4-(α-Methylbenzyl)-1,2,4-triazoline-3,5-dione (119) with Tetrahydrofuran (THF)

S-(-)-4-(α-methylbenzyl)-1,2,4-triazoline-3,5-dione (1.00 g, 4.92×10^{-3} mole) was placed in a 50 ml round-bottomed flask, and 20 ml of THF was added. The deep-pink solution was stirred by a magnetic stirrer, and the flask was fitted with a water-cooled condenser. The flask was heated by means of a heating mantel, and the pink solution was refluxed for 8 hours. At the end of the refluxing period, a pale-yellow solution was obtained. The excess THF was removed by rotary evaporation, and the pale-yellow viscous oil remaining was dried in a vacuum desiccator at 65°C for several hours. The yield was 1.30 g (96%, based on one-to-one adduct). This viscous oil solidified upon standing at room temperature. Fractional crystallization from diethyl ether yielded a white solid, m.p. 122-124°C.

IR (KBr) 3430 (w), 3120 (s), 2975 (m), 2935 (m), 2900 (w), 1760 (s), 1690 (s), 1580 (m), 1490 (m), 1440 (s), 1380 (s), 1340 (w), 1256 (w), 1240 (w), 1210 (m), 1260 (m), 1070 (s), 1045 (m), 1025 (m), 980 (m), 966 (m), 925 (m), 785 (m), 770 (m), 725 (m), 700 (s), 620 (m), 610 (m) cm^{-1}.

^1H NMR (DMSO-d_6, TMS) δ 1.75 (d, 3H, J = 7.3 Hz), 2.00 (m, 4H), 3.73 (m, 2H), 5.19 (q, 1H, J = 7.4 Hz), 5.70 (dist. t, 1H), 7.34 (s, 5H), 10.23 (s, br, 1H).

^{13}C NMR (DMSO-d_6, TMS, int. ref. DMSO-d_6) 17.28, 17.42, 24.54, 27.85, 49.73, 49.93, 68.64, 85.61, 85.65, 126.50, 127.47, 128.45, 140.39, 140.53, 154.32, 154.47.

^{13}C NMR - off resonance (DMSO-d_6, TMS, int. ref DMSO-d_6): 17.40 (q, CH_3, J = 42.75 Hz), 24.59 (t, CH_2, J = 43.88 Hz), 27.90 (t, CH_2, J = 45.08), 49.83 (d, CH, J = 63.35 Hz), 68.29 (t, CH_2, J = 58.50 Hz), 85.65 (d, CH, J = 78.00 Hz), 126.57 (d, CH, J = 81.62 Hz), 127.52 (d, CH, J = 82-85), 128.47 (d, CH, J = 84.00 Hz), 140.53 (s, -C=), 154.35 (s, -C=)

$[\alpha]_D^{25}$ -51.8° (C = 10.0, CH_2Cl_2).

Synthesis of Optically Active Polymers

Modification of Polydienes with S-(-)CTD (119)

Cis-1,4-polybutadiene was obtained from Aldrich Chemical Co. 1,2-Syndiotactic polybutadiene and polybutadiene liquid, 85% vinyl 1,2 content (M.W. 2000), were purchased from Polysciences, Inc.

Modification of cis-1,4-polybutadiene at 5% conversion: Percentage of S-(-)CTD was added based on molar repeating unit of the polydienes. Into a 250 ml Erlenmeyer flask, 1.00 g (0.0185 mole) of cis-1,4-polybutadiene was dissolved in 100 ml of toluene. A solution of 0.1878 g (0.000924 mole) of S-(-)-4-(α-methylbenzyl)-1,2,4-triazoline-3,5-dione in 10 ml of toluene was added all at once at room temperature. The pink color disappeared in less than 8 minutes. The colorless solution was stirred at room temperature overnight, then was concentrated to a volume of 50 ml and added slowly to 200 ml of 95% ethanol containing 0.5% of 2,6-di-tert-butyl-4-methylphenol (BHT) as antioxidant. The polymer was dried in a vacuum desiccator for 24 hours at room temperature to give 1.072 g (90.2%) of white-to-clear rubbery material.

At 10% conversion: 2.00 g of the cis-1,4-polybutadiene was dissolved in 40 ml of toluene. S-(-)CTD (0.751 g) in 15 ml of toluene was added. The reaction was complete in about 30 minutes. 95% ethanol was used as a non-solvent reagent. The modified polymer is a white, rubbery material; yield is 87.2%.

At 20% conversion: 1.00 g of polydiene was dissolved in 150 ml of toluene. S-(-)CTD (0.751 g) in 20 ml of toluene was added. After 4 hours, the deep-pink color of S-(-)CTD faded. The modified polymer was insoluble in toluene in this case and was removed from the solvent and dried under vacuum to yield 1.60 g (91.4%) of rubbery, pale-yellow material.

At 30% conversion: 1.00 g of cis-1,4-polybutadiene was dissolved in 150 ml of toluene. S-(-)CTD (1.13 g) in 30 ml of toluene was added all at once. The color of S-(-)CTD disappeared after 4 days. A mass of polymer precipitated after addition of S-(-)CTD. The modified polymer was removed from the solvent and dried to yield 1.70 g (80.0%) of rubbery material.

At 50% conversion: 1.00 g of polydiene was dissolved in 100 ml of toluene. S-(-)CTD (1.88 g) in 25 ml of toluene was added, and a precipitate formed immediately. DMSO (50 ml) was added. The deep-pink color disappeared in about 6 hours. Ethanol (95%) was used as a non-solvent reagent. The modified polymer is a brittle solid.

At 100% conversion: 1.00 g of cis-1,4-polybutadiene was dissolved in 400 ml of THF. A solution of 3.75 g of S-(-)CTD in 60 ml of toluene was added dropwise over a period of 9 hours. The characteristic color of S-(-)CTD faded after 24 hours. The modified polymer

is soluble in THF. The pale-yellow solution was concentrated to about 50 ml and was added slowly into 300 ml of anhydrous diethyl ether containing 0.5% of 2,6-di-tert-butyl-4-methylphenol (BHT) as antioxidant. A white solid was obtained and dried to yield 3.65 g (81.0%) of off-white powder, softening point 163°C.

IR (KBr) 3450 (m, br), 3220 (m, br), 3060 (w), 3040 (w), 2940 (w), 1765 (s), 1700 (s), 1500 (w), 1430 (s), 1380 (m), 1250 (w, br), 1160 (w), 1090 (w), 1050 (w), 1030 (m), 980 (m), 760 (m), 700 (m), 610 (m) cm^{-1}.

Modification of 1,2-Syndiotactic Polybutadiene at 100% Conversion

Into a 500 ml three-necked, round-bottomed flask equipped with a mechanical stirrer, water-cooled condensar attached to a drying tube containing silica gel and thermometer was placed 0.50 g (9.24 x 10^{-3} mole) of 1,2-syndiotactic polybutadiene and 200 ml of methylene chloride. The flask was heated by means of a heating mantel, and the stirrer was started. The mixture was refluxed overnight, during which time the polymer completely dissolved. 5-(-)-4-(α-methylbenzyl)-1,2,4-triazoline-3,5-dione (1.88 g, 9.24 x 10^{-3} mole) was added in one portion. The deep-pink solution was refluxed for 26 hours, after which a pale-yellow solution was obtained. Refluxing was continued for 48 hours. The methylene chloride was removed by rotary evaporation, and a yellow solid remained which was dried to yield 2.40 g (100%) of a pale-yellow solid. This solid was dissolved in 20 ml of methylene chloride and then slowly dropped into 300 ml of diethyl ether containing 0.5% of BHT as antioxidant. A white precipitate was obtained, filtered and dried to give a white solid (1.80 g, 75%), softening point 185°C.

IR (KBr): 3460 (m, br), 3200 (m, br), 3060 (m), 3030 (m), 2980 (m), 2930 (m), 1765 (s), 1700 (s), 1490 (m), 1420 (s), 1380 (s), 1210 (m), 1160 (m), 1070 (w), 1050 (m), 1025 (m), 990 (m), 910 (m), 830 (m), 760 (m), 700 (s), 610 (m) cm^{-1}.

Polybutadiene, 85% vinyl 1,2 content ($\overline{M}_W$ 2000), was also modified at 100% conversion with S-(-)CTD in methylene chloride at 40°C by the same procedure as above. A white solid was obtained after purification from the methylene chloride/ether system. A 75% yield was obtained after purification, softening point 167°C. The IR (KBr) spectrum is exactly the same as the 1,2-syndiotactic polybutadiene modified at 100% conversion.

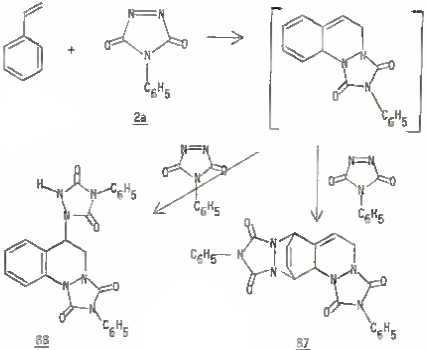
CHAPTER III

RESULTS AND DISCUSSION

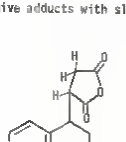
Background

In 1967, Cookson, Gilani and Stevens[35] reported that 4-phenyl-1,2,4-triazoline-3,5-diene (2b) reacts with styrene and leads to a double Diels-Alder adduct, 87. Reinvestigation of this reaction by Wagener, Turner and Butler[77] revealed that the Diels-Alder-ene adduct, 88, was also formed in approximately a 2-1 ratio of 88 to 87 (Scheme XVI)

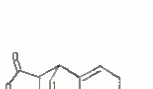
Scheme XVI



This reaction is similar to the case in which styrene reacts with maleic anhydride[78] in a Diels-Alder-ene fashion to yield 2 1 adducts 89 and 90. Ethyl azobisformate[4] also reacts with styrene to give adducts with similar structures:



89



90

Wagener, Turner and Butler[77] also investigated the reaction of styrene with bis-triazolinediones which lead to the formation of copolymers containing both double Diels-Alder and Diels-Alder-ene repeating units. This was the first example of a propagation mechanism involving predominantly a Diels-Alder-ene reaction sequence. A kinetic and mechanistic investigation of such a copolymerization was carried out by Lal.[79]

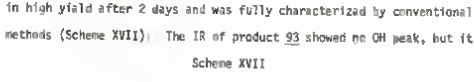
The first aim of this research was to find a suitable plasticizer for the development of a new elastomeric impression material using bis-triazolinedione as a cross-linking agent. Eugenol is a naturally occurring product. It has been used in perfumery as a substitute for oil of cloves, in manufacturing vanillin, in preparation of zinc oxide dental cements, etc. For our purposes, isoeugenol (2-methoxy-4-propenylphenol, 91) was selected as a potential plasticizer, since it has

a functionality of three and can be incorporated into the cross-link polymerization. Therefore, it was important to evaluate its reactivity with bis-triazolinedione.

Reaction of Isoeugenol with Methylisocyanate

In general, triazolinediones react with hydroxyl groups, thus, it became necessary to protect the hydroxyl group of isoeugenol. Although the reaction of isoeugenol 91 with isocyanate has been reported,[71] no experimental details are available. Isoeugenol 91 was allowed to react with an excess of methylisocyanate, 92, in ligorin in the presence of triethylamine as catalyst. The product precipitated in high yield after 2 days and was fully characterized by conventional methods (Scheme XVII). The IR of product 93 showed no OH peak, but it

Scheme XVII



91 92 93

had a peak at 3320 cm^{-1} which corresponded to an N-H peak, it also showed carbonyl peaks at 1738 and 1714 cm^{-1} due to dimerization via hydrogen bonding and resonance effects. The ^{13}C NMR spectrum showed carbonyl carbon at 154.79 ppm and CH_3-N at 27.14 ppm. The ^{13}C NMR spectrum of compound 93 is shown in Figure 1.

Detailed investigations of the isocyanate-hydroxyl reaction have been reported by Baker and coworkers [80-83]. The base catalyzed reaction is thought to follow the mechanism shown in Scheme XVIII.

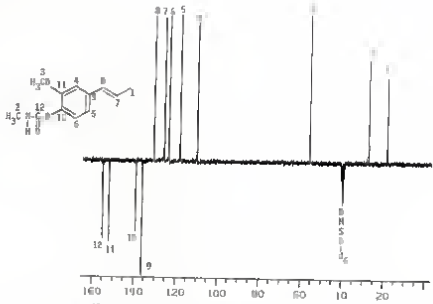
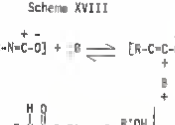


Figure 1 75 MHz ^{13}C NMR spectrum of compound **93** using multiplicity determination sequence (CH_3, CH pos CH_2, C neg) in DMSO-d_6 at 25°C

Scheme XVIII



Model Compound Studies

For most polymers except those with very simple structures, the NMR spectra generally are complicated and broad. Therefore, it would be difficult to determine their structure by NMR alone. However, with the aid of well-defined model compounds, structure determination of polymers can be made much easier.

For the first part of this research, two new model compounds were synthesized. These model compounds are derived via reaction of 2-methoxy-4-propenylphenyl methylcarbamate (93) with MeTD (2a) and PhTD (2b). 4-Ph and Me triazolinediones were prepared[10,69] (Scheme XIX).

When compound 93 was allowed to react with 2a, the deep-pink color of MeTD disappeared in less than 40 seconds with an exothermic reaction. A white precipitate was formed after a few hours. Recrystallization from H_2O-EtOH gave white crystals with a melting point of 211-215°C. Elemental analysis was consistent with a 1:2 adduct. ^1H NMR analysis showed a peak at 10.21 ppm which is a singlet and was assigned to the N-H protons of the urazole moiety. This peak disappeared when D_2O was added. Peaks at δ 7.98 ppm and 7.96 ppm were

0 = CH_3 96, R = C_6H_5 98

0 = CH_3 95, R = C_6H_5 97

assigned to aromatic protons; peaks at 2.92 ppm and 3.02 ppm were assigned to two non-equivalent methyl groups. The ^{13}C NMR spectrum showed five non-equivalent carbonyl groups at 148.00, 148.16, 153.77, 153.93 and 154.06 ppm. Peaks at 110.26 ppm and 114.31 ppm were assigned to the methine carbon of the aromatic ring. The spectral evidence is consistent with the Diels-Alder-ene adduct structure 95. The mother liquor from the first filtration was evaporated, leaving a small amount of pale-yellow solid. IR and NMR spectra of this compound were almost identical to those of compound 95, with some impurity, which was less than 2% and was assumed to be double Diels-Alder adduct 96. Therefore, reaction of compound 93 with MeTD (2a) leads to one product (D A-ene adduct) almost exclusively. The ^{1}H NMR and ^{13}C NMR spectra of compound 95 are shown in Figures 2, 3, 4 and 5.

4-Phenyl-1,2,4-triazoline-3,5-dione (2b) also was allowed to react with compound 93. The red color of PhTD disappeared in less than 30 seconds with an exothermic reaction. After about 3 minutes, a white precipitate formed. The white solid was recrystallized from 95% ethanol to give shiny, colorless crystals that had a melting point of 188-191°C. Elemental analysis was in agreement with a 1:2 adduct. The ^{1}H NMR spectrum (Figure 6) showed a peak at 10.78 ppm which was assigned to the N-H proton of the urazole moiety; this peak also disappeared upon addition of one drop of D_2O to the NMR tube. Peaks at 7.14 ppm and 8.07 ppm were assigned to the aromatic proton attached adjacent to the methoxy group and the proton attached next to the urethane group, respectively. The peak at 7.74 ppm is a distorted quartet and was assigned to the N-H proton of the urethane group.

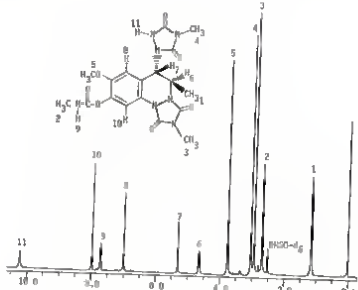


Figure 2 ^{1}H NMR (300 MHz) spectrum of model compound 9b in DMSO-d_6 at 85°C

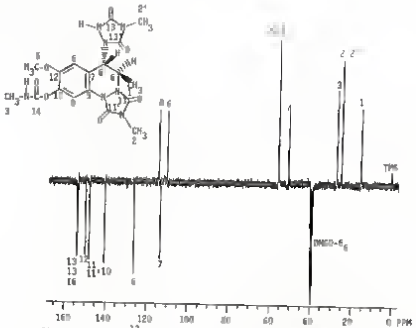


Figure 3 75 MHz ^{13}C NMR spectrum of model compound 66 - using multiplicity determination sequence (CH, CH_3 pos; CH_2 + C neg) in DMSO-d_6 at 85°C

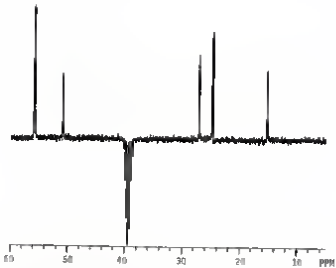


Figure 4 Expanded regions of the 75 MHz ^{13}C NMR spectrum of model compound 85.

Figure 5 Expanded regions of the 75 MHz ^{13}C NMR spectrum of model compound 95

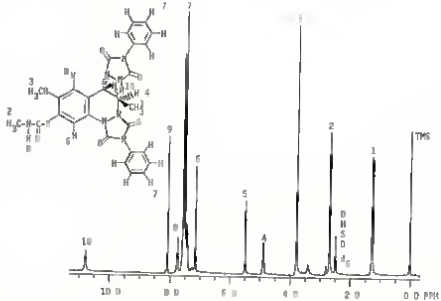


Figure 8 ^{1}H NMR (300 MHz) spectrum of model compound 9Z in DMSO-d_6 at 25°C

This peak disappears slowly with addition of D_2O. The ^{13}C NMR spectra (Figures 7 and 8) showed peaks at 110.78 ppm and 114.54 ppm which were assigned to the protonated carbons of the fused aromatic ring. The peaks at 55.92 ppm and 113.68 ppm were assigned to the methine carbon attached to the aromatic ring and the quaternary carbon of the aromatic ring attached to the methine carbon, respectively. Based on the ^1H NMR and ^{13}C NMR analyses, it is clear that this crystalline solid is formed via a Diels-Alder-ene sequence. Thus, structure 97 was assigned to the compound (Scheme XIX). The mother liquor from the first filtration gave a small amount of yellow solid which, based on the IR and NMR spectra, had a structure similar to compound 97, with a small amount of impurities (~3%). These impurities could have been formed via a double Diels-Alder reaction pathway, 98. Thus, reaction of 4-PhTD with compound 93 is stereoselective and leads to essentially one product. Although the Diels-Alder reaction occurs faster than the ene reaction, the activation energy for an ene reaction is higher than that for the analogous Diels-Alder reaction. However, steric and electronic effects could and will change this behavior. As can be seen in this case, when compound 93 reacts with 4-PhTD and 4-MeTD, the first step of the reaction is the Diels-Alder reaction (the faster one). The second step of the reaction can occur either by an ene pathway or by the Diels-Alder reaction. However, two factors will favor an ene reaction pathway. First, the bulky groups of the methyl urethane and methoxy will prevent the approach of the second mole of triazolinedione for the Diels-Alder attack. Second, the rearomatization of the diene ring favors the ene process. Therefore, steric and

Figure 7 75 MHz ^{13}C NMR spectrum of model compound 97, using multiplicity determination sequence (CH, CH_3 pass; CH_2, C neg) in DMSO-d_6 at 25°C

Figure 8 Expanded regions of the 75 MHz ^{13}C NMR spectrum of model compound 52

electronic factors favor the formation of only the Diels-Alder-ene adducts 95 and 97. The ^1H NMR and ^{13}C NMR data of compounds 96 and 97 are summarized in Tables I and II.

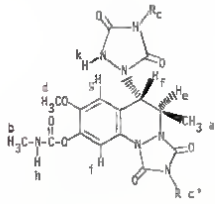
Synthesis and Identification of Bis-triazolinediones

Two bis-triazolinediones, 1,6-bis-(3,5-dioxo-1,2,4-triazoline-4-yl)hexane (108) and bis-(p-3,5-dioxo-1,2,4-triazoline-4-ylphenyl)-methane (109), were selected for this study. These bis-triazoline-diones were synthesized by the method developed by Turner,[74] Wegener[77] and Saville[51] with some modifications. The reactions are shown in Scheme XX.

Bis-triazolinedione 108 was prepared in four steps. One mole of 1,6-hexane diisocyanate (99) was allowed to react with two moles of ethylhydrazine carboxylate[6,69] (101) in benzene at 10°C. A voluminous white slurry formed after 2 minutes, and a white solid was obtained in almost quantitative yield after filtration and drying. This compound was characterized by IR, ^1H NMR and ^{13}C NMR, and no further purification was necessary. Cyclization of compound 102 was performed with a fresh solution of sodium ethoxide at reflux temperature. The disodium salt (104) was isolated as a light-yellow solid. As had been reported[77] previously, compound 104 was converted to its acidic form, 106, in low yield using concentrated hydrochloric acid. A new method was developed in order to achieve higher yield. Thus, 95% ethanol was added to the pale-yellow solid, 104, which was then acidified with glacial acetic acid to give a clear, yellowish solution. Addition of methylene chloride and cooling in a freezer furnished a white solid;

TABLE 1

^{1}H NMR Data[a] for Model Compounds 95 and 97



R = CH_3 95

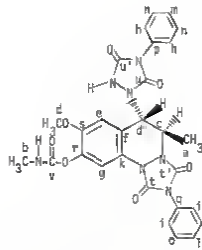
R = C_6H_5 97

Protons	R = CH_3	J, Hz	R = C_6H_5	J, Hz
a	1.14 (d, 3H)	6.30	1.26 (d, 3H)	6.60
b	2.67 (d, 3H)	4.50	2.68 (d, 3H)	4.50
c	2.92 (s, 3H)	-	7.46 (m, 10H)	-
c'	3.02 (s, 3H)	-		
d	3.74 (s, 3H)	-	3.78 (s, 3H)	-
e	4.63 (m, 1H)	-	4.87 (m, 1H)	-
f	5.29 (d, 1H)	1.80	5.48 (br, 1H)	-
g	6.98 (s, 1H)	-	7.13 (s, 1H)	-
h	7.69 (q, 1H)	4.80	7.74 (q, 1H)	4.80
i	7.96 (s, 1H)	-	8.07 (s, 1H)	-
k	10.21 (s, 1H)	-	10.78 (s, 1H)	-

[a] Solvent DMSO-d_6, Int. Ref. TMS. Values reported in δ units. Abbreviations used are s = singlet, d = doublet, q = quartet, m = multiplet, br = broad.

Table 11

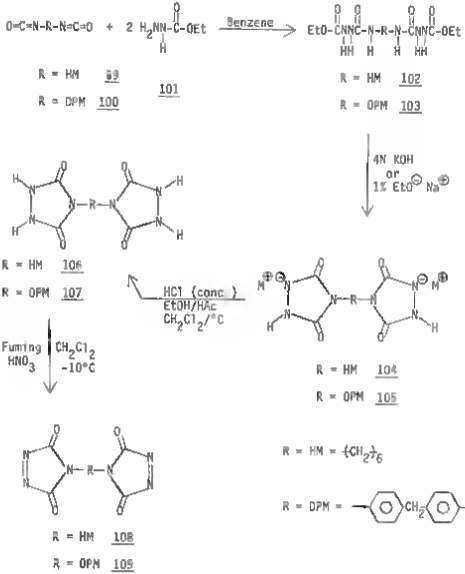
^{13}C NMR Data[a] for Model Compounds 95 and 97



Carbon	R = C_6H_5	R = CH_3	Carbon	R = C_6H_5	R = CH_3
a	15.41	15.24	n	128.81	-
b	27.11	27.11	o	128.94	-
c	50.75	50.31	p	131.02	-
d,d'	55.32	55.73, 55.85	q	131.47	-
e	110.78	110.26	r	140.80	140.61
f	113.68	113.46	s	147.11	150.02
g	114.54	114.31	t	148.32	148.00
h	126.16	-	t'	148.61	148.16
i	126.36	-	u	152.20	153.77
k	126.31	126.35	u'	152.41	153.97
l	127.96	-	v	153.97	154.06
m	128.28	-			

[a] Solvent DMSO-d_6, Int. Ref. DMSO-d_6, 39.5 ppm. Values reported in ppm units.

Scheme XX


Benzene
R = HM 99
R = DPM 100
101
R = HM 102
R = DPM 103
4N KOH
or
1% EtO⊖ Na⊕
R = HM 106
R = DPM 107
HCl (conc.)
EtOH/HAc
CH2Cl2/°C
R = HM 104
R = DPM 105
Fuming HNO3
CH2Cl2
-10°C
R = HM 108
R = DPM 109
R = HM = (CH2)6
R = DPM =
CH2

Recrystallization from hot water gave white crystals. The elemental analysis is in agreement with the assigned structure, 106. The IR of the pale-yellow solid, 104, showed two carbonyl peaks at 1695 and 1600 cm^{-1}, whereas that of compound 106 showed only one carbonyl peak at 1685 cm^{-1}. The ^1H NMR spectrum of compound 106 showed a peak at 1.40 ppm which was assigned to the four methylene protons (C_2-C_5) The peaks at 3.36 ppm (triplet) were assigned to the methylene protons attached to the nitrogen atom of the urazole ring. The peak at 5.77 ppm was assigned to the protons attached to the nitrogen atom. The ^{13}C NMR spectrum showed a peak at 26.56 ppm which was assigned to the C_2 and C_5 carbons; the peak at 27.56 ppm was assigned to the C_3 and C_5 carbons; the peak at 37.94 ppm was assigned to the C_1 and C_6 carbons, the peak at 155.26 ppm was assigned to the carbonyl groups. Oxidation of compound 106 with fuming nitric acid at -10°C gave a light-pink solid. Purification was achieved by dissolving the pink solid in ethyl acetate and slowly dropping the solution into cyclohexane. Elemental analysis of the pink solid was in agreement with the assigned structure, 108.

Bis-triazolinedione 109 was prepared by a similar procedure to 108, except bis-urazole 107 was synthesized via cyclization of compound 103 with 4 N potassium hydroxide followed by acidification with concentrated hydrochloric acid. The dipotassium salt, 105, was not isolated in this case.

The ^1H NMR spectrum of compound 107 showed a peak at 4.00 ppm which was assigned to the methylene protons; a peak at 7.39 ppm (m) was assigned to the aromatic protons, a peak at 10.43 ppm was assigned

to the N-H protons. The ^{13}C NMR spectrum in DMSO-d_6 showed a peak at 40.11 ppm which was assigned to the methylene carbon. The peak at 125.97 ppm was assigned to the ortho carbons of the aromatic rings. The peak at 128.96 ppm was assigned to the meta carbons, the peak at 129.84 ppm was assigned to the para carbons; the peaks at 140.46 ppm were assigned to the carbons attached to the nitrogen atoms. The peak at 153.43 ppm was assigned to the carbonyl carbons.

Oxidation of compound 107 was performed by two methods. In Method A, bis-urazole 107 was oxidized by gaseous dinitrogentetroxide in the presence of anhydrous sodium sulfate in methylene chloride at -6°C. After workup, a red solid was obtained. Further purification was accomplished by dissolving the solid in ethyl acetate and precipitating into n-hexane. In Method B, oxidation was achieved by use of fuming nitric acid, and purification was accomplished similarly to that of Method A. The yield in the latter case was much lower. Data on the yield, melting point and purification procedures are shown in Table III.

Synthesis and Characterization of Copolymers

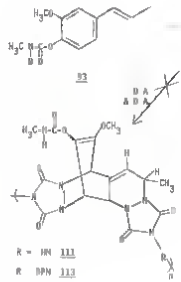
The second aim of this investigation was to evaluate the reactivity of compound 93 with bis-triazolinediones 108 and 109. Thus, equal moles of compound 93 in N,N-dimethylformamide (DMF) were allowed to react with bis-triazolinedione 108 at room temperature. The reaction (Scheme XXI) was spontaneous, fast, and highly exothermic. The deep-pink colored solution of bis-triazolinedione 108 disappeared in less than 40 seconds. The polymer that formed was soluble in DMF. The pale-yellow solution, after stirring for 48 hours at room

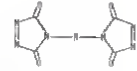
Table III

Data on Yield, Melting Points, and Purification
For The Synthesis of Bis-triazolinediones

R	Compound	Yield %	Melting Points °C	From
HM	102	100	202-203	-
DPM	103	94	253-256	-
HM	104	100	>300	-
DPM	105 was not isolated			
HM	106	75	223-224	H_2O
DPM	107	94	>300	$MeOH-H_2O$
HM	108	60	146-148	EtAC/
DPM	109	84	>186d	EtAC/ n-hexane

Scheme XXI


93
D A
& D A
D A
& ENE
R = HM 111
R = BPM 113
R = HM 110
R = BPM 112


R = HM 106
R = BPM 109

temperature, was added dropwise to diethyl ether, resulting in a white precipitate. Further purification was achieved by dissolving the white solid in DMF and precipitation into diethyl ether. This procedure was repeated twice. The white solid was dried in a vacuum oven at 90°C for 48 hours to ensure complete removal of DMF. The copolymer is a white solid and is soluble in dimethylsulfoxide (DMSO), DMF, $CHCl_3$ and slightly soluble in ethanol, ethyl acetate, and methanol. The reaction of compound 93 with bis-triazolinedione 109 was also spontaneous, fast and highly exothermic, the reaction was performed in DMF. The red color changed to pale-yellow in less than 35 seconds. The copolymer remained soluble in DMF and was precipitated into ether. The resulting copolymer was an off-white solid and is soluble in highly polar solvents such as DMSO and DMF. It is insoluble in ethanol, acetone and ethyl acetate, but slightly soluble in THF.

The copolymers prepared from bis-triazolinediones 108 and 109 and compound 93 were characterized by IR, ^{13}C NMR, ^{1}H NMR, viscometry, membrane osmometry (MO), and differential scanning calorimetry (DSC) in order to determine the microstructures, molecular weights and thermal stabilities of the copolymers.

The microstructures of the copolymers were determined mainly by ^{1}H NMR and ^{13}C NMR spectroscopy, since the IR spectra of the copolymers did not give much structural information because of overlap of IR absorption peaks. The assignments of the NMR peaks of the copolymers were made possible by comparing the spectra with those of appropriate model compounds synthesized in this investigation. From this comparison, it became clear that in both cases copolymers 110 and 112

with only Diels-Alder-ene repeating units were formed, and copolymers 111 and 113 with double Diels-Alder repeating units were not formed. The ^{1}N NMR spectrum (Figure 9) in DMSO-d_6 showed a peak at 3.42 ppm which was assigned to the four methylene groups of C_2-C_5. The peak at 6.95 ppm was assigned to the aromatic proton next to the methoxy group. The peak at 7.96 ppm was assigned to the aromatic proton next to the urethane group. The peak at 10.26 ppm was assigned to the N-H proton of the urazole moiety.

The ^{13}C NMR spectrum (Figure 10) of copolymer 110 showed a peak at 25.44 ppm which was assigned to C_3 and C_4 methylene carbons. The peak at 27.21 ppm was assigned to C_2 and C_5 methylene carbons. The peak at 39.11 ppm was assigned to C_1 and C_6 methylene carbons. The peak at 110.32 ppm was assigned to the aromatic methine carbon next to the methoxy group. The peak at 114.04 ppm was assigned to the aromatic methine carbon next to the urethane group. The peaks at 147.85, 148.00, 153.58, 153.94, and 154.73 ppm were assigned to 5 carbonyl carbons.

The ^{1}N NMR spectrum (Figure 11) of copolymer 112 showed a peak at 7.09 ppm which was assigned to the aromatic methine proton next to the methoxy group. The peak at 8.02 ppm was assigned to the aromatic methine proton next to the urethane group. The peaks at 7.42 ppm were assigned to the aromatic protons of the diphenyl methane group. The peak at 10.56 ppm was assigned to the N-H proton of the urazole moiety.

The ^{13}C NMR spectrum (Figure 12) of compound 112 showed all peaks which are in agreement with the assigned structure 112. Complete data on ^{1}N NMR and ^{13}C NMR of compounds 110 and 112 are shown in Tables IV and V, respectively.

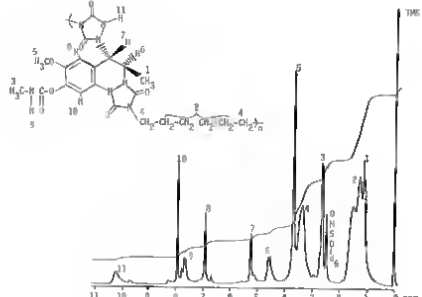


Figure 9 ^{1}H NMR (100 MHz) spectrum of copolymer 13D, in DMSO-d_6 at 25°C

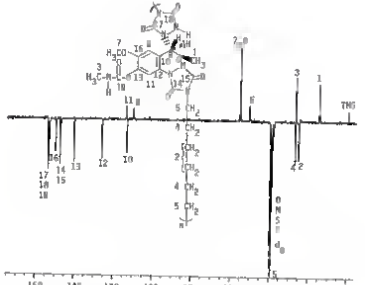


Figure 10. ^{13}C NMR (75 MHz) spectrum of copolymer XIII using multiplicity determination sequence (CH, CH_3 pos, CH_2 neg) in DMSO-d_6 at 25°C.

Figure 12 ^{1}H NMR (100 MHz) spectrum of copolymer 112 in DMSO-d_6 at 25°C

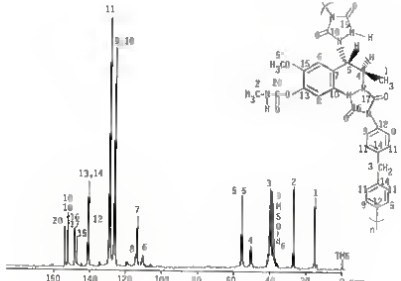
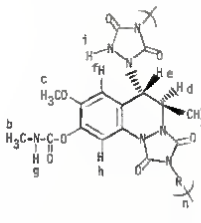


Figure 12 ^{1}H decoupled ^{13}C NMR (25 MHz) spectrum of copolymer 11c in DMSO-d_6 at 25°C

Table IV

^{1}H NMR Data[a] for Copolymers 110 and 112



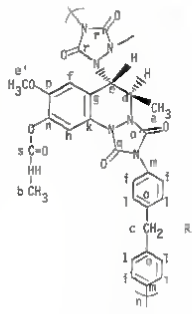
Protons	R = HM	J, Hz	R = DPM	J, Hz
a	1.12 (d, 3H)	6.2	1.21 (d, 3H)	5.9
b	2.66 (d, 3H)	4.4	2.66 (d, 3H)	4.1
c	3.72 (s, 3H)	-	3.76 (s, 3H)	-
d	4.61 (m, 1H)	-	4.78 (m, br, 1H)	-
e	5.27 (br, 1H)	-	5.42 (s, br, 1H)	-
f	6.95 (s, 1H)	-	7.09 (s, 1H)	-
g	7.69 (m, 1H)	-	7.68 (m, 1H)	-
h	7.96 (s, 1H)	-	8.02 (s, 1H)	-
i	10.28 (br, s, 1H)	-	10.56 (s, br, 1H)	-

[a] Solvent DMSO-d_6, int ref TMS. Values reported in δ units. Abbreviations used are s = singlet, d = doublet, m = multiplet, and br = broad.

Table V

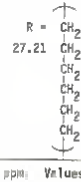
^{13}C NMR Data[a] for Copolymers 110 and 112

Carbon	R = OPM	R = HM
a	15.47	15.06
b	27.22	27.21
c	40.38	–
d	50.95	50.94
e,e'	56.07	56.71, 55.82
f	106.87	110.32
g	113.82	113.49
h	114.40	114.04
i	126.40	–
k	126.55	126.30
l	129.27	–
m	129.66	–
n	140.87	140.63
o	141.26	–
p	147.21	150.17
q	148.38	147.85
q'	148.82	148.00
r	152.33	153.58
r'	152.57	153.94
s	154.08	154.13



R = OPM = 112

R = HM = 110



[a] Solvent DMSO-d_6, int. ref. DMSO-d_5, 39.5 ppm. Values reported in ppm units

Table VI

Differential Scanning Calorimetry (DSC) Data[a]
For Copolymers 110 and 112

R	MM	OPM
T_g °C	186	-
T_{cd} °C	-	264
T_c °C	206	-
T_m °C	232	-
T_d °C	252	310

T_g = glass transition temperature

T_{cd} = chemical degradation temperature

T_c = crystallization temperature

T_m = melting temperature

T_d = decomposition temperature

[a] Data obtained by taking the average of several measurements

The intrinsic viscosities ([η]) of copolymers 110 and 112, measured in N,N-dimethylformamide at 30°C, were found to be 0.206 and 0.205 dl/g, respectively. These viscosities indicate that some degree of polymerization had occurred during the chemical reactions.

The thermal behavior of the copolymers was measured by using differential scanning calorimetry (DSC) and is summarized in Table VI. The two copolymers have different thermal behavior. Copolymer 110, with R = hexamethylene, shows four different thermal changes. It has a glass transition state at lower temperature, then it crystallizes at higher temperature. It melts after crystallization, and it decomposes at very high temperature. Copolymer 112, with R = DPM, however, does not have glass transition state, rather it undergoes chemical degradation, and decomposes at an elevated temperature.

Synthesis and Characterization of Optically Pure R-(+) and S-(-)-4-(α-Methylbenzyl)-1,2,4-triazoline-3,5-dione

The first aim of the second part of this research was to synthesize the N-4-chiral-substituted triazolinediones. Optically active pure α-methylbenzylamine is commercially available, therefore, optically active pure triazolinediones should be readily prepared from this amine by a series of chemical transformations. At the same time, we proposed to synthesize this triazolinedione. Paquette and Doehner[76] reported a procedure for the syuthesis of S-(-)-4-(α-methylbenzyl)-1,2,4-triazoline-3,5-dione (119).

In our case, some modificatieus in the reported procedure[76] were necessary in order to obtain adequate quantities for this investigation. Thus, S-(-)-α-methylbenzylamine (114) was allowed to react with

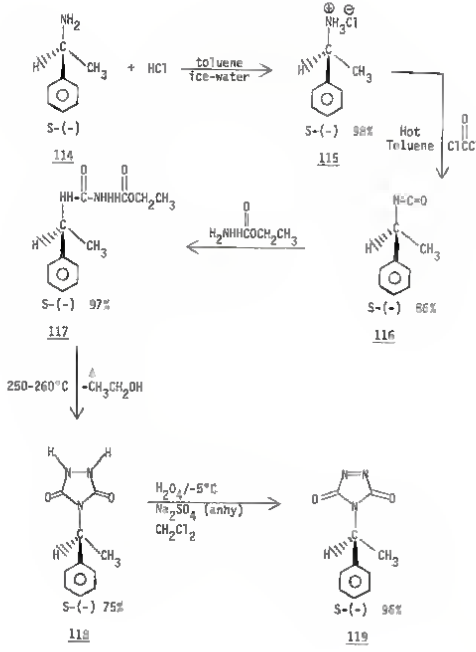
dry hydrogen chloride gas in one cycle, and a quantitative yield of the amine salt (115) was collected (Scheme XXII). This amine salt melts at 169.0-170.0°C. No further purification was necessary.

The amine salt (115) was converted to the S-(-) isocyanate (116) via passing phosgene gas through a slurry mixture of hot toluene, which resulted in a high yield (86%) of compound 116. It is a clear, colorless liquid, lachrymator, moisture sensitive, and it must be handled with care. The IR spectrum of compound 116 shows a strong stretching vibration band at 2260 cm^{-1}, which is a characteristic absorption of the isocyanate (-N=C=O) group. The ^1H NMR spectrum (Figure 13) of this compound in $CDCl_3$ showed peaks at 1.69 ppm, which is a doublet and were assigned to methyl protons. The peaks at 4.75 ppm are a quartet and were assigned to C-H proton. The peak at 7.34 ppm was assigned to the aromatic protons.

The S-(-) isocyanate (116) was treated with ethyl carbazate to afford S-(-) semicarbazide 117 in a quantitative yield (97%). This semicarbazide had been reported[76] as an oily substance, however, in our case, it was isolated as a white solid, having a melting point of 87.0-89.0°C. No further purification was performed on this compound.

The ^1H NMR spectrum (Figure 14) of compound 117 showed peaks at 1.16 ppm (triplet) assigned to methyl protons of the ethoxy group. The peaks at 1.35 ppm (doublet) were assigned to CH_3 protons attached to the benzylic carbon. The peaks at 4.03 ppm (quartet) were assigned to the methylene protons of the ethoxy group. The peaks at 4.80 ppm (pentate) were assigned to the benzylic proton. The peaks at 6.73 ppm

Scheme XXII


NH2
CH3
+ HCl
toluene
ice-water
S-(-)
114
NH3 Cl
S-(-) 98%
115
Hot
Teluene
ClCCl
HH-C-NHHHCOCH2CH3
S-(-) 97%
117
H2NHHCOCH2CH3
N=C=O
S-(-) 86%
116
250-260°C
-CH3CH2OH
H2O2/-5°C
Na2SO4 (anhy)
CH2Cl2
S-(-) 75%
118
S-(-) 96%
119

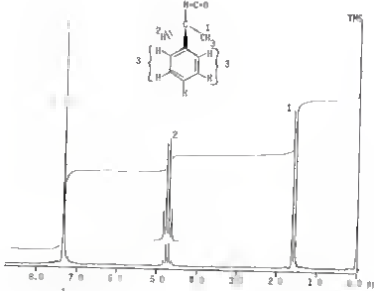


Figure 13 ^{1}H NMR (100 MHz) spectrum of compound 116 in $CDCl_3$ at 25°C

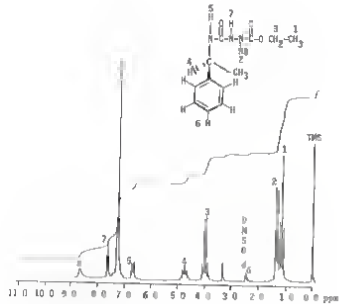


Figure 14 ^{1}H NMR (100 MHz) spectrum of compound 117, in DMSO-d_6 at 25°C

(doublet) were assigned to the NH proton attached to the benzylic carbon. The peaks at 7.67 and 9.72 ppm were assigned to the two NH protons.

The ^{13}C NMR spectrum (Figure 15) showed two peaks for carbonyl carbons at 156.96 and 157.48 ppm. The peak at 14.50 ppm was assigned to the methyl carbon of the ethoxy group. The peak at 60.36 ppm was assigned to the methylene carbon of the ethoxy group.

Cyclization of compound 117 was performed by heating at 250-260°C in a sand bath. The crystalline product 119 was isolated in high yield (75%) from a hot solution of benzene rather than by trituration in petroleum ether.[76] The residue became very tough after pyrolysis, was difficult to triturate, and a poor yield was obtained. Compound 119 was purified by recrystallization from benzene.

Oxidation of S-(-) urazole 119 with dinitrogen tetroxide gave an excellent yield of the S-(-) triazolinedione 119 with a higher melting point and specific rotation than previously reported.[76] Further purification can be achieved via sublimation under vacuum. The ^{1}H NMR spectrum (Figure 16) of compound 119 shows no peak at 9.97 ppm which is indicative of the absence of N-H protons. The ^{13}C NMR spectrum of compound 119 in DMSO-d_6 is shown in Figure 17. All of the above compounds were fully characterized by using IR, ^{1}H NMR, ^{13}C NMR and mass spectra. R-(+)CTD was also prepared by a similar procedure.

The visible spectra of S-(-)-4-(α-methylbenzyl)-1,2,4-triazoline-3,5-dione (119) were recorded in selected solvents, as shown in Figure 18 and Table VII. Three $\lambda_{max's}$ were exhibited in toluene and methylene chloride, whereas only two $\lambda_{max's}$ were exhibited in more polar

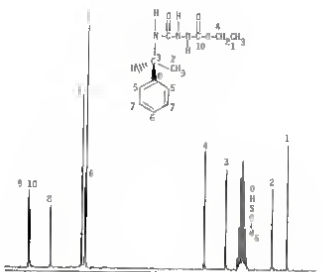


Figure 15 ^{1}H decoupled ^{13}C NMR (25 MHz) spectrum of compound **117** in DMSO-d_6 at 25°C

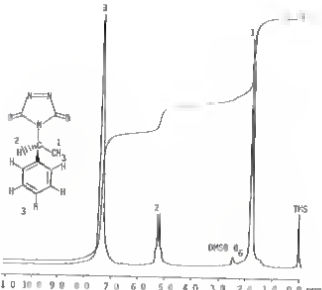


Figure 16 ^{1}H NMR (300 MHz) spectrum of compound 21a in DMSO-d_6 at 25°C.

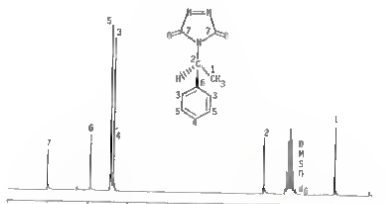


Figure 17 ^{1}H decoupled ^{13}C NMR (25 MHz) spectrum of compound 119, in DMSO-d_6 at 25°C

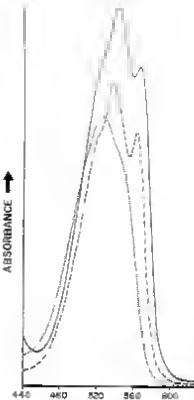


Figure 18 Visible spectra of 5-(-)-4-(α-methylbenzyl)-1,2,4-triazoline-3,5-dione (TAD) in toluene (—), methylene chloride (– –) and acetone (· · ·) at 25°C.

Table VII

Visible Absorption of S-(-)-4-(α-Methylbenzyl)-1,2,4-triazoline-3,5-dione (119) in Selected Solvents at 25°C

Solvent	λ_{max} nm	ε
Toluene	565,542,525 (sh)	148,185,149
CH_2Cl_2	566,538,526 (sh)	116,146,114
Acetone	540 (sh), 525	100,122
THF	540 (sh), 530	105*,116*
DMSO	530 (sh), 520	117*,137*
DMF	540 (sh), 520	76*,84*

*Estimated value Because of the instability of 5-(-)-triazolinedione in THF, DMSO and DMF

solvents such as tetrahydrofuran (THF), dimethylsulfoxide (DMSO), and dimethylformamide (DMF). In the toluene, methylene chloride and acetone cases, molar absorptivity (ε) are true values. However, in the THF, DMSO and DMF cases, they are only estimated values, since absorption changes with time due to interaction of compound 119 with the solvents

Kinetics Study for Decomposition of S-(-)-4-(α-Methylbenzyl)-1,2,4-triazoline-3,5-dione (119) in Different Solvents at 25°C

Since selection of the solvent was very important for the modification of polydienes because of the solubility problem, it became necessary to evaluate the stability of compound 119 in selected solvents. Six solvents (methylene chloride, toluene, acetone, THF, DMSO and DMF) were selected. Solutions of known concentration (6.57×10^{-3} M) of compound 119 in these solvents were prepared. One milliliter of the solution was put in a U.V. cell, and absorbances were recorded for time intervals of 10 minutes or 60 minutes. In the toluene, methylene chloride and acetone cases, no appreciable change in absorbance occurred after several hours. These results indicated that compound 119 is quite stable in these solvents at room temperature. In the THF, DMSO and DMF cases, absorbances decreased with time. The data are shown in Tables VIII, IX and X.

Plots of $\% A/A_0$ versus time in different solvents are shown in Figures 19 and 20. Compound 119 decomposes to the extent of 13.96% in one hour in DMF, whereas its rate of decomposition is 0.72% and 0.62% per hour, respectively, in THF and DMSO. From this investigation, it is evident that compound 119 is more stable in less polar

Table VIII

Time Variation of Visible Absorbance of Compound 119 in DMF

t_{min}	A	-Ln A	A/A_o
0	0.5323*	0.6305	1.0000
10	0.5310	0.6330	0.9976
20	0.5130	0.6675	0.9637
30	0.4950	0.7032	0.9299
40	0.4800	0.7340	0.9014
50	0.4580	0.7793	0.8792
60	0.4580	0.7809	0.8604
70	0.4480	0.8030	0.8416
80	0.4395	0.8221	0.8257
90	0.4305	0.8428	0.8087
100	0.4230	0.8604	0.7966
110	0.4152	0.8790	0.7800
120	0.4080	0.8965	0.7665

*A_o was obtained from Y intercept of plot -Ln A vs. time

Table IX

Time Variation of Visible Absorbance of Compound 119 in THF

t_{hr}	A	-Ln A	A/A_o
0	0.3593*	1.0236	1.0000
1	0.3567	1.0309	0.9928
2	0.3462	1.0606	0.9635
3	0.3367	1.0887	0.9371
4	0.3283	1.1137	0.9137
5	0.3217	1.1342	0.8953
6	0.3162	1.1512	0.8800
7	0.3100	1.1712	0.8628
8	0.3050	1.1874	0.8489
9	0.3000	1.2040	0.8349
10	0.2960	1.2174	0.8238

*A_o was calculated from Y intercept of plot -Ln A vs time

Table X

Time Variation of Visible Absorbance of Compound 119 in DMSO

t_{hr}	A	-Ln A	A/A_o
0	0.4025*	0.9101	1.0000
1	0.4000	0.9163	0.9938
2	0.3950	0.9289	0.9814
3	0.3913	0.9384	0.9722
4	0.3875	0.9480	0.9627
5	0.3833	0.9589	0.9523
6	0.3813	0.9643	0.9473
7	0.3775	0.9742	0.9379
8	0.3750	0.9809	0.9317
9	0.3725	0.9875	0.9255
10	0.3688	0.9976	0.9163

*A_o was obtained from Y intercept of plot -Ln A vs. time

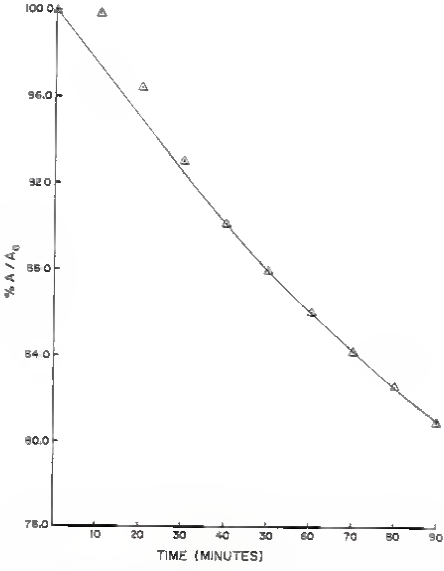


Figure 19. Decomposition of S-(-)-4-(α-methylbenzyl)-1,2,4-triazoline-3,5-dione (113) in DMF at 25°C as shown by % A/A_0 vs. time curve.

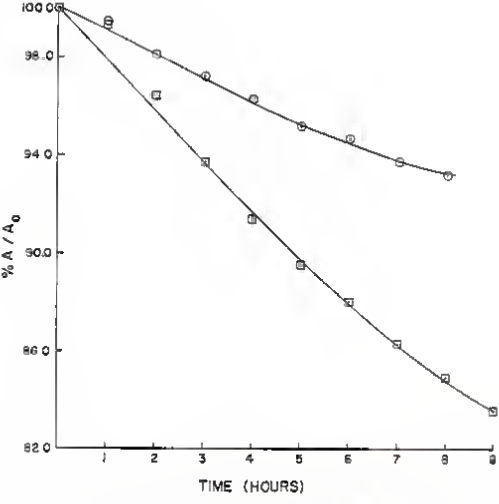


Figure 20 Decomposition of S-(-)-4-(α-methylbenzyl)-1,2,4-triazoline-3,5-dione (119) in THF (⊡) and DMSO (⊕) at 25°C as shown by % A/A_0 vs. time curve.

solvents and less stable in more polar solvents, thus, it is better to use methylene chloride or toluene as a solvent for chemical transformation where it is possible.

Since in the above study the solvents are in great excess, the above data were used in the following equation and were treated according to pseudo-first-order kinetics.

$$\text{Ln } A_o/A_t = kt, \quad t_{\frac{1}{2}} = \frac{\text{Ln } 2}{k}$$

where A_o = initial absorbance, A_t = absorbance at time = t, $t_{\frac{1}{2}}$ = half-life, and k = rate constant. The plot of -Ln A vs. time gave a straight line in all cases (Figures 21,22,23). The rate constants and $t_{\frac{1}{2}}$ were calculated using the method of least-squares and are shown in Table XI.

From this study, we became interested in investigating the reaction of compound 119 with THF. Thus, a solution of compound 119 in THF was refluxed for several hours. After about 8 hours, a pale-yellow solution was obtained. Fractional crystallization from diethyl ether gave a white solid with a melting point of 122-124°C (Scheme XXIII).

The product (120) was characterized by IR, ^{1}H NMR and ^{13}C NMR. The ^{1}H NMR spectrum of compound 120 (Figure 24) in DMSO-d_6 shows peaks at 2.00 ppm (multiplet) which were assigned to the methylene groups (four protons) of the THF ring. The peaks at 3.73 ppm (multiplet) were assigned to the methylene protons next to the oxygen atom. The peaks at 5.70 ppm (dist. triplet) were assigned to the methine proton on the THF ring. The peak at 10.23 ppm (singlet) was assigned to the N-H proton.

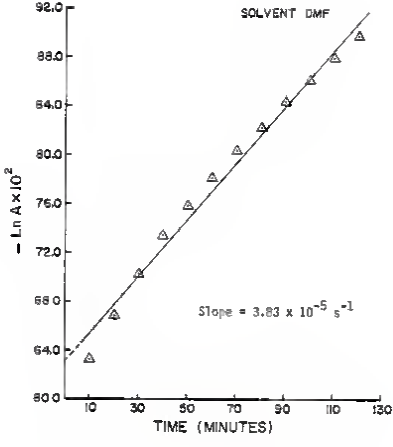


Figure 21. Pseudo-first-order plot of decomposition of compound 119, in DMF at 25°C.

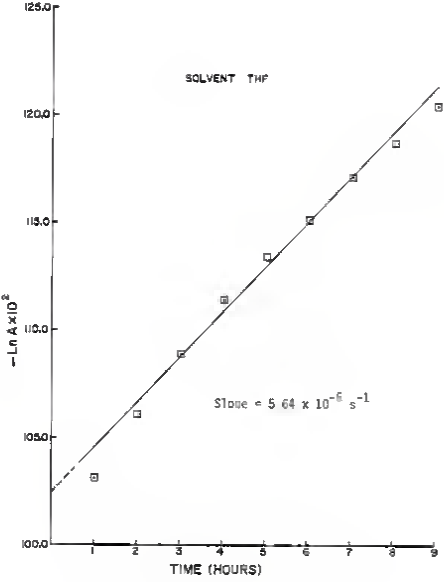


Figure 22. Pseudo-first-order plot of decomposition of compound 11@, in THF at 25°C.

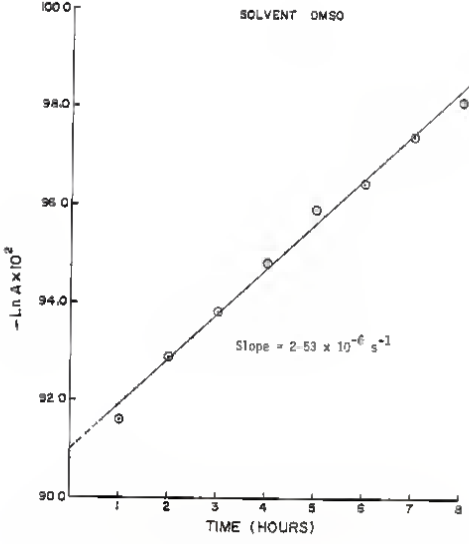


Figure 23. Pseudo-first-order plot of decomposition of compound 115 in DMSO at 25°C

Table XI

The Pseudo-First-Order Kinetics for Decomposition of S-(-)-4-(α-Methylbenzyl)-1,2,4-triazoline-3,5-dione (119) in Different Solvents at 25°C

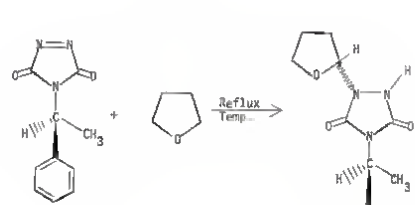
Solvent	k s^{-1}	$t_{\frac{1}{2}}$ hr	COC[b]
DMF	3.83 x 10^{-5}	5.02	0.9909
THF	5.64 x 10^{-6}	34.10	0.9926
DMSO	2.53 x 10^{-6}	76.20	0.9961

[a] Calculated by the method of least-squares.

[b] COC = correlation coefficient

Figure 24 ^{1}H NMR (100 MHz) spectrum of compound 12c in DMSO-d_6 at 25°C

Scheme XXIII



S-(-)

119

SR & SS

120

The ^{13}C NMR spectrum (Figure 25) shows peaks at 17.28 and 17.42 ppm which were assigned to the CH_3 carbon attached to the benzylic carbon. The peaks at 49.73 and 49.93 ppm were assigned to the methine carbon of the benzylic carbon. The peaks at 85.61 and 85.65 ppm were assigned to the methine carbon (asymmetric center) attached to the nitrogen atom of the urazole moiety. The peaks at 140.38 and 140.53 ppm were assigned to the quaternary carbon of the aromatic ring. From the above information, it became evident that the reaction of THF with compound 119 yielded two diastereomers, SR and SS, in a ratio of about 50:50. This indicated that the hydrogen abstraction and addition reaction occurred in a non-stereospecific fashion. The off-resonance spectrum (Figure 26) was used to assign the CH_2 and CH peaks.

Figure 25. ^{1}H decoupled ^{13}C NMR (25 MHz) spectrum of compound 120 in DMSO-d_6 at 25°C

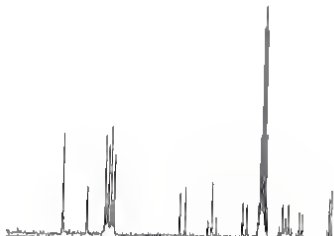


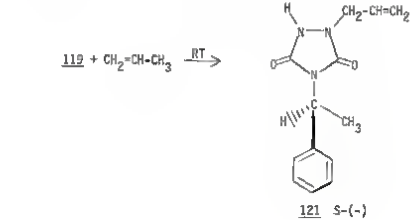
Figure 26 Off resonance ^{13}C NMR (25 MHz) spectrum of compound 170 in $DMSO-d_6$ at 25°C

Recently, Wamhoff and Wald[84] reported the reaction of PhTD with THF thermally as well as photochemically. In the thermal reaction, two products, mainly the hydrogen abstracting addition adduct, but also the dimerization product of PhTD, were isolated. However, in this case, the reaction of S-(-) CTD 119 with THF yielded only the hydrogen abstraction addition adduct 120.

Model Compounds Studies

As was mentioned previously, in the synthesis of polymers it is very useful to prepare appropriate model compounds and fully characterize them. Since the spectral data of polymers are usually complicated, the second aim of this study was to prepare proper model compounds and fully identify them. Thus, S-(-) CTD 119 was allowed to react with propylene at room temperature (Scheme XXIV). The pink color faded in about 4 hours. A white solid was obtained from slow evaporation of the ethereal solution. Further purification was achieved via sublimation under vacuum. The product (121) has a melting point of 73.5-76.0°C.

Scheme XXIV



121 S-(-)

The ^{1}H NMR spectrum (Figure 27) of compound 121 shows peaks at 4.03 ppm (doublet) which were assigned to the methylene protons attached to the urazole moiety. The peak at 10.49 ppm was assigned to the N-H proton. The peaks at 5.2 ppm (multiplet) were assigned to vinylic CH_2 and benzylic CH protons.

The ^{13}C NMR spectrum (Figure 28) of compound 121 shows a peak at 48.4 ppm which was assigned to the methylene carbon attached to the nitrogen atom of the urazole ring. The peak at 119.0 ppm was assigned to the $=CH_2$ carbon. The peak at 131.5 ppm was assigned to the vinylic methine carbon.

Another model compound was synthesized by reaction of S-(-) CTD 119 with 1,5-hexadiene. A solution of 119 in methylene chloride was allowed to react with a large excess of 1,5-hexadiene (30:1 molar ratio). After disappearance of the deep-pink color and evaporation of the solvent, an oily substance was obtained. Purification was performed via column chromatography using silica gel, which yielded a pale-yellow liquid (Scheme XXV). The ^{1}H NMR and ^{13}C NMR spectra (Figures 29 and 30) are in agreement with the formation of a 1:1 ene adduct 122.

The ^{1}H NMR spectrum shows peaks at 2.75 ppm (triplet) which were assigned to the methylene protons between the two vinyl groups. The peaks at 3.97 ppm (doublet) were assigned to the methylene protons attached to the nitrogen atom.

The ^{13}C NMR spectrum shows a peak at 47.67 ppm which was assigned to the methylene carbon attached to the nitrogen atom. The peak at 35.58 ppm was assigned to the methylene carbon between the two

Figure 27 ^{1}H NMR (300 MHz) spectrum of compound 121 in DMSO-d_6 at 25°C

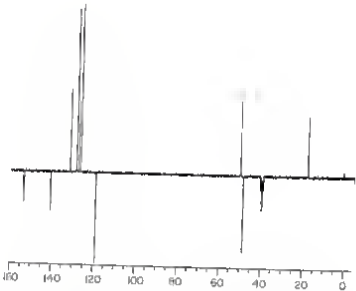
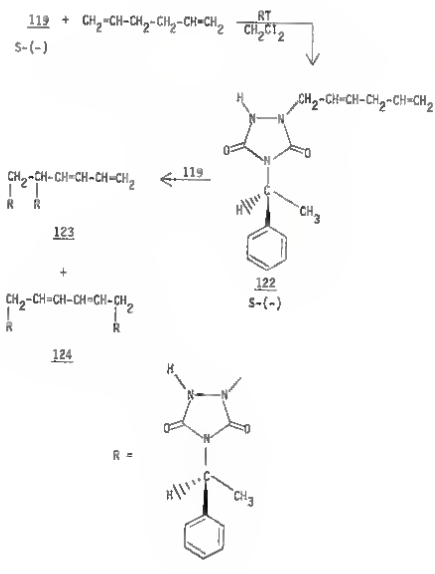


Figure 28 75 MHz ^{13}C NMR spectrum of compound 121 using multiplicity determination sequence (CH, CH_3 pos; CH_2, C neg) in DMSO-d_6 at 25°C

Scheme XXV


119
S-(-)
RT
CH_2Cl_2
CH_2-CH=CH-CH_2-CH=CH_2
119
CH_2-CH-CH=CH-CH=CH_2
R R
123
+
CH_2-CH=CH-CH=CH-CH_2
R R
124
122
S-(-)
R =

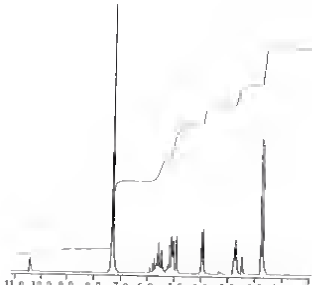


Figure 29 ^{1}H NMR (100 MHz) spectrum of compound I22 in DMSO d_6 at 25°C

Figure 30 75 MHz ^{13}C NMR spectrum of compound 122 using multiplicity determination sequence (CH_3, CH pos. CH_2, C neg) in DMSO d_6 at 25°C

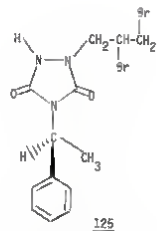
vinyl groups. The peak at 115.70 ppm was assigned to the terminal methylene carbon.

When 1 mole of 1,5-hexadiene was allowed to react with 2 moles of compound 119, a white solid was obtained. The NMR analysis of the white substance showed that it contains an adduct of 1:2 mole ratio of structure 123 predominantly, and compound 124 was not observed and apparently did not form at all.

X-Ray Crystallographic Analysis of S-(-)-4-(α-Methylbenzyl)-1-(2,3-dibromopropyl)urazole

The third aim of this study was to identify the nature of the intermolecular N-H bonding in the solid state of the chiral urazole moiety and relate this interaction to the change in properties of the modified polymers. It was also necessary to confirm the absolute configuration of the chiral substituent on the 4-position of the triazoline moiety, and that no racemization had occurred during the series of reactions used for synthesis. Thus, model compound 121 was selected for this study.

Although compound 121 is a solid and can be purified by sublimation, it has a low melting point. Therefore, it was suggested that this compound be brominated, since it would be easier to do x-ray analysis on the compound containing heavy atoms. Bromination of compound 121 was performed by use of a solution of Br_2 in CCl_4 at room temperature to yield compound 125. This compound was purified by recrystallization from methanol, and its structure was characterized by IR, ^1H NMR and ^{13}C NMR.



125

Crystals suitable for X-ray studies were grown by slow evaporation of a methanol solution. All measurements were carried out using a $P\bar{1}$ diffractometer with Zr-filtered MO radiations $\lambda\alpha_1$ = 0.70926 and $\lambda\alpha_2$ = 0.71354 Å. Pertinent crystal data and other details are given in Table XII. The crystal structure was solved by the heavy atom method and refined by least-squares techniques [95]

The absolute configuration was determined using the anomalous dispersion effect of the two bromine atoms. After three cycles of least-squares using isotropic thermal parameters, the R values ($R = \Sigma||Fo|-|Fc||/\Sigma|Fo|$) for the two possible configurations were 0.106 and 0.096. With anisotropic thermal parameters for only the two Br atoms, the R value was 0.073. Least-squares refinement using the block approximation and anisotropic thermal parameters for all atoms gave a final R value of 0.066

Table XII

Crystal Data for S-(-)-4-(α-Methylbenzyl)-1-(2,3-dibromopropyl)urazole (125)

Formula	$C_{13}H_{15}O_2N_3Br_2$
Molecular Weight	405.10
Space Group	$P2_12_12_1$
a, Å	5.985(2)
b, Å	10.758(3)
c, Å	23.063(3)
α, deg	90*
β, deg	90*
γ, deg	90*
Volume, Å^3	1484.8(6)
Z	4
D_m, g cm^{-3}	1.807
D_c, g cm^{-3}	1.812
Crystal Size, mm	0.27 x 0.27 x 0.13
μ, cm^{-1}	54.1
Radiation Used	Mo Kα-graphite monochromator
2θ Range	0-46°
No. of Measured Reflections	1183
No. of Reliable Reflections	986
K [in I < Kσ(I)]	2.0
Goodness of Fit	0.257
R	0.066

* Required by symmetry of space group.

The final positional parameters and the hydrogen atom positions are given in Tables XIII and XIV, respectively. The final thermal parameters are shown in Table XV. A difference Fourier synthesis gave reasonable positions for twelve of the fifteen hydrogen atoms in the molecule.

A drawing illustrating the atomic numbering used in the X-ray analysis is given in Figure 31. The computer-generated ORTEP drawing and stereoscopic view of compound 125 are given in Figures 32 and 33, respectively. Bond distances and angles for the non-hydrogen atoms are presented in Tables XVI and XVII, respectively. Selected torsion angles are given in Table XVIII. The observed and calculated structure factors appear in Appendix 1.

The five-membered triazoline ring is distorted from planarity towards the envelope conformation. The puckering amplitude[86] was estimated to be 0.056 Å from the observed torsion angle. The small puckering angle is undoubtedly due to the two C=O groups which tend to limit the puckering of the ring. The two Br atoms are essentially trans relative to the C(7)-C(8) bond, as would be expected on steric grounds. The dihedral angle between the phenyl ring and the five-membered ring is 65.8°.

The distances in the triazoline structure are similar to the dimensions observed in semicarbazones and related compounds.[87] There is a lengthening of the C(2)-O(1) bond compared to that of C(5)-O(2) which could be related to the N-H···O hydrogen bond to O(4). However, the distances are not significantly different, so the effect may not

Table XIII

Final Positional Parameters ($\times 10^4$) and Their Estimated Standard Deviations for S-(-)-4-(α-Methylbenzyl)-1-(2,3-dibromopropyl)urazole (125)

ATOM	X	Y	Z
BR(1)	-6454(4)	-1255(2)	-1888(1)
BR(2)	-724(4)	-3104(2)	-683(1)
O(1)	-4348(25)	-1840(12)	-3089(5)
O(2)	-9442(24)	-4954(12)	-2742(6)
N(1)	-7339(27)	-3226(14)	-3030(6)
N(3)	-4513(27)	-3523(15)	-2429(7)
N(4)	-6193(29)	-4338(13)	-2258(6)
C(2)	-5308(33)	-2750(17)	-2877(7)
C(5)	-7910(33)	-4284(18)	-2695(8)
C(6)	-3059(32)	-3008(18)	-1987(8)
C(7)	-4250(35)	-2535(19)	-1442(8)
C(8)	-2713(39)	-1839(19)	-1018(8)
C(9)	-8903(38)	-2798(18)	-3478(7)
C(10)	-8947(42)	-1288(23)	-3520(9)
C(11)	-9589(38)	-3415(17)	-4053(7)
C(12)	-8560(38)	-3319(20)	-4325(8)
C(13)	-8247(43)	-3872(20)	-4912(8)
C(14)	-8002(44)	-4515(21)	-5131(8)
C(15)	-10010(42)	-4652(17)	-4965(8)
C(16)	-10323(38)	-4118(18)	-4292(9)
H(4)	-651	-514	-220
H(7)	-645	-362	-138
H(9)	-1038	-325	-327
H(12)	-543	-277	-429
H(14)	-733	-486	-553
H(16)	-1163	-435	-388
H(81)	-158	-373	-184
H(81)	-188	-128	-128
H(82)	-389	-154	-60
HM(1)	-943	-66	-320
HM(2)	-1053	-127	-377
HM(3)	-723	-124	-378

Table XIV

The Hydrogen Atom Positions (x 10^3)
From the Final Difference Fourier for
S-(-)-4-(α-Methylbenzyl)-1-(2,3-dibromopropyl)urazole (125)

ATOM	x	y	z
H(4)	-941	-514	-220
H(7)	-845	-362	-136
H(9)	-1026	-325	-327
H(12)	-843	-277	-429
H(14)	-732	-464	-553
H(16)	-1142	-435	-348
H(61)	-185	-373	-164
H(61)	-148	-126	-126
H(62)	-349	-154	-60
HW(1)	-903	-66	-320
HW(2)	-1053	-127	-377
HW(3)	-728	-124	-376

Table XV

Final Thermal Parameters (x 10^4) for S-(-)-4-(α-Methylbenzyl)-1-(2,3-dibromopropyl)urazole (125)

The Form of the Thermal Parameter is

$$\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$$

ATOM	U11	U22	U33	U12	U13	U23
BR(1)	41(1)	34(1)	30(2)	15(1)	6(1)	-1(1)
BR(2)	54(1)	51(1)	36(2)	0(1)	-19(1)	10(1)
O(1)	44(9)	25(7)	25(7)	-14(8)	-1(7)	-1(6)
O(2)	30(8)	33(8)	41(8)	-13(8)	-8(7)	7(7)
N(1)	23(8)	26(6)	16(8)	3(8)	-4(7)	6(7)
N(3)	15(9)	49(12)	34(10)	13(10)	-6(8)	3(9)
N(4)	40(11)	16(7)	27(9)	1(9)	-17(9)	3(7)
C(2)	25(11)	23(10)	17(10)	2(9)	5(9)	-4(8)
C(5)	30(12)	15(9)	26(11)	0(10)	13(10)	-12(9)
C(6)	25(11)	33(11)	23(10)	0(11)	-16(9)	-16(10)
C(7)	26(11)	32(11)	25(10)	6(11)	-1(10)	-6(9)
C(8)	56(14)	31(11)	16(10)	13(13)	-3(11)	7(10)
C(9)	44(14)	36(12)	19(10)	12(12)	6(10)	7(9)
C(10)	56(17)	59(14)	39(13)	0(17)	4(13)	-1(12)
C(11)	30(11)	34(12)	13(9)	9(11)	-9(9)	10(9)
C(12)	32(13)	54(14)	19(10)	9(12)	3(11)	-3(11)
C(13)	71(17)	43(13)	22(11)	18(16)	4(13)	12(11)
C(14)	66(17)	5)(14)	15(11)	-8(15)	5(12)	-16(11)
C(15)	48(17)	13(11)	29(12)	7(12)	-7(12)	-2(9)
C(16)	26(11)	35(13)	40(12)	-9(10)	-1)(11)	-4(11)

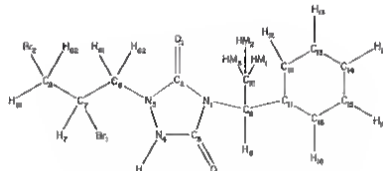


Figure 31 Numbering scheme used in X ray analysis of 5-(-) 4-(α-methylbenzyl)-1-(2,3-dibromopropyl)urazole (125)

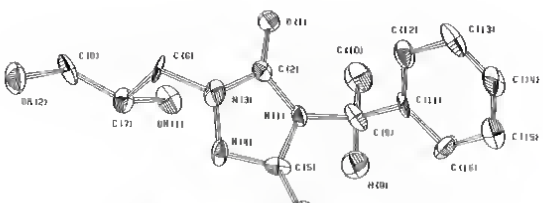


Figure 32 An ORTEP view of S-(-) 1-(α-methylbenzyl)-1 (2,3-dibromopropyl)ureazole showing the atomic numbering and thermal ellipsoids (50% probability level). Only the hydrogen atom on C(4) is shown with the other hydrogen atoms being omitted for clarity

Figure 33 Stereoscopic view of S-( ) 4-(α-Methylbenzyl) 1-(2,3-dibromopropyl)urazole (125)

Table XVI

Bond Distances (Å) With Their Estimated Standard Deviations For S-(-)-4-(α-Methylbenzyl)-1-(2,3-dibromopropyl)urazole (125)

C(11) - C(12)	1.361(29)
C(12) - C(13)	1.491(26)
C(13) - C(14)	1.355(34)
C(14) - C(15)	1.358(34)
C(15) - C(16)	1.454(28)
C(16) - C(11)	1.405(28)
C(11) - C(9)	1.495(24)
C(9) - C(10)	1.527(32)
C(9) - N(1)	1.469(25)
N(1) - C(2)	1.366(25)
C(2) - N(3)	1.408(24)
N(3) - N(4)	1.393(23)
N(4) - C(5)	1.444(25)
C(5) - N(1)	1.400(23)
C(2) - O(1)	1.236(22)
C(5) - O(2)	1.185(23)
N(3) - C(6)	1.451(24)
C(6) - C(7)	1.532(26)
C(7) - C(8)	1.538(28)
C(7) - Br(1)	1.990(21)
C(8) - Br(2)	1.985(21)

Table XVII

Bond Angles (Deg) With Their Estimated Standard Deviations For S-(-)-4-(α-Methylbenzyl)-1-(2,3-dibromopropyl)urazole (125)

C(11)-C(12)-C(13)	120.0(18)	N(1)-C(2)-N(3)	105.5(15)
C(12)-C(13)-C(14)	116.4(20)	C(2)-N(3)-N(4)	109.8(16)
C(13)-C(14)-C(15)	125.0(21)	N(3)-N(4)-C(5)	106.1(14)
C(14)-C(15)-C(16)	118.8(19)	N(4)-C(5)-N(1)	104.9(15)
C(15)-C(16)-C(11)	118.2(18)	C(5)-N(1)-C(2)	112.0(15)
C(16)-C(11)-C(12)	121.3(18)	O(1)-C(2)-N(3)	127.0(17)
C(12)-C(11)-C(9)	119.6(17)	O(2)-C(5)-N(4)	126.4(17)
C(16)-C(11)-C(9)	119.1(17)	C(2)-N(3)-C(6)	119.5(15)
C(11)-C(9)-C(10)	113.2(16)	N(4)-N(3)-C(6)	116.1(15)
C(11)-C(9)-N(1)	113.6(16)	N(3)-C(6)-C(7)	115.1(16)
C(10)-C(9)-N(1)	111.4(16)	C(6)-C(7)-C(8)	113.9(16)
C(9)-N(1)-C(2)	129.2(16)	C(6)-C(7)-Br(1)	107.7(13)
C(9)-N(1)-C(5)	118.9(15)	C(8)-C(7)-Br(1)	104.0(13)
N(1)-C(2)-O(1)	127.5(17)	C(7)-C(8)-Br(2)	106.7(13)
N(1)-C(5)-O(2)	129.7(17)		

Table XVIII

Selected Torsion Angles (Deg) For
S-(-)-4-(α-Methylbenzyl)-1-(2,3-dibromopropyl)urazole (125)

Atoms	Angle
N(1)-C(2)-N(3)-N(4)	-8.8
C(2)-N(3)-N(4)-C(5)	13.0
N(3)-N(4)-C(5)-N(1)	-12.0
N(4)-C(5)-N(1)-C(2)	7.0
C(5)-N(1)-C(2)-N(3)	0.8
N(4)-N(3)-C(6)-C(7)	-45.3
N(3)-C(6)-C(7)-C(8)	-172.2
Br(1)-C(7)-C(8)-Br(2)	172.1
C(5)-N(1)-C(9)-C(10)	142.7
C(5)-N(1)-C(9)-C(11)	-88.1
C(12)-C(11)-C(9)-N(1)	-59.0
C(16)-C(11)-C(9)-N(1)	119.1
C(12)-C(11)-C(9)-C(10)	69.3
C(16)-C(11)-C(9)-C(10)	-112.7

be real. The ring distances appear to reflect the difference in substitution on N(3) versus N(4), as well as the lengthening of the C(2)-O(1) bond. Unfortunately, the presence of the two bromine atoms has reduced the accuracy of the determination so that the differences are not significant based on the usual tests.

From this study, it is clear that the absolute configuration is S and that no racemization had occurred during the course of the seven-step synthesis.

Synthesis and Characterization of Optically Active Polymers

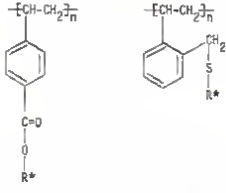
Background

Optically active homopolymers as well as copolymers have been prepared and are reported in the literature.[85-98] d-s-Butyl p-vinylbenzoate[89] and o-vinylbenzyl d-s-butyl sulfide[90] have been polymerized via free radical initiation using benzoyl peroxide and α,α'-azobisisobutyronitrile as initiators. The resulting polymers (126 and 127) (Scheme XXVI) are optically active and showed specific rotations of +22.9° and +9.69°, respectively, in benzene. In both cases, when the original centers of asymmetry were removed, no optical activity remained.

S-α-Methylbenzyl methacrylate[91] was polymerized with α,α'-azobisisobutyronitrile as initiator to poly-s-α-methylbenzyl methacrylate (128). This polymer was further treated with phosphonium iodide to give polymethacrylic acid, which showed no optical activity at all. S-α-Methylbenzyl methacrylate was copolymerized with maleic anhydride. The resulting copolymer (129) was optically active. Removal of the S-α-methylbenzyl group with phosphonium iodide left a copolymer which was optically active

Scheme XXVI

Optically Active Polymers

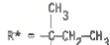


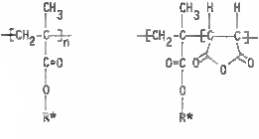
126

$[\alpha]_D^{50}$ +22.9° (benzene)

127

$[\alpha]_0^{24.7}$ +9.59° (benzene)





128

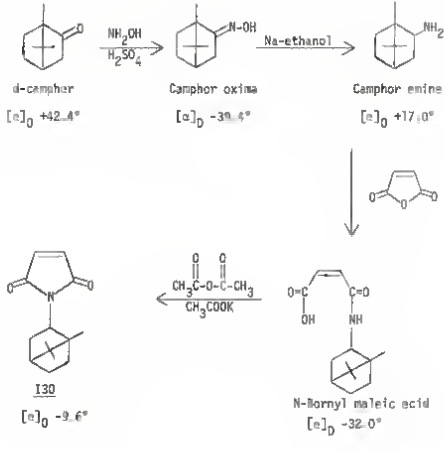
$[\alpha]_0^{25}$ -77.4°

129

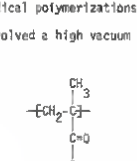
$[\alpha]_0^{25}$ -50.2°

Optically active n-bornyl maleimide[93] (130) was synthesized with d-camphor amine and maleic anhydride (Scheme XXVII). Polymerizations of n-bornyl maleimide were performed with benzoyl peroxide, α,α'-azobisisobutyronitrile and n-butyllithium. The resulting polymers were optically active. Copolymerizations of optically active n-bornyl maleimide with vinyl monomers were carried out with the use of a radical initiator, and optically active copolymers were obtained.

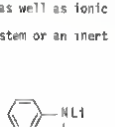
Scheme XXVII



Optically active anionic catalysts have been used for the asymmetric polymerizations [37]. Triphenylmethyl methacrylate (TrMA) has been polymerized with two types of asymmetric anionic initiators, lithium(R)-N-(1-phenylethyl)anilide (LiAn) and (-)-sparteine-butyllithium complex (Sp-BuLi), at -78°C. Both catalysts gave optically active polymers. The polymers obtained with Sp-BuLi in toluene showed a positive specific rotation and increased with polymer yield reaching above +300°. The polymers resulting from LiAn in toluene and THF showed specific rotations $[\alpha]_0^{20}$ from -50° to -90° (in THF). Free-radical polymerizations, as well as ionic polymerizations, usually involved a high vacuum system or an inert atmosphere.



PTrMA



LiAn

Sp-BuLi

Modification of Polydienes via the Ene Reaction with Triazolinediones

A variety of enophiles such as N-methylmaleimide, maleic anhydride, chloromaleic anhydride, γ-crotonolactone, fumaric acid, p-benzoquinone, acrylonitrile, maleic acid, and tetrahydrophthalic anhydride have been studied as modifiers for diene polymers both by radical-initiated and thermal reactions [39]. Although the radical-initiated

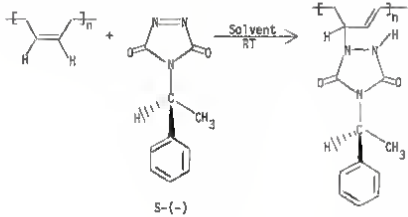
reactions are more effective at lower temperatures, up to 22% conversion, they are accompanied by unfevorable radical-initiated side reactions such as chain scission and crosslinking. The thermal reaction, assumed to proceed by the electrocyclic ene mechenism, resulted in an extent of reaction of only about 12%. Temperatures up to a maximum of 240°C, however, must be used with this reaction to obtain this extent of addition. Higher temperatures that increase the extent of addition are accompanied by depolymerization.

Butler and coworkers[100-102] have studied the ene reaction of 4-Ph and 4-Me-1,2,4-triazoline-3,5-diones with preformed diene polymers and copolymers such as random cis-trans-polybutadiene, cis-polybutadiene, random styrene (45%)-butadiene, 1:1 alternating copolymer of furen end maleic enhydride, styrene-butadiene ABA block copolymer, 25% styrene (SBS) and styrene-butadiene random copolymer, styrene-isoprene block copolymer, 15% styrene-poly-cis-isoprene, polyacrylonitrile-co-butadiene, and poly-1,2-butadiene to synthesize a series of new polydienes. The reactions occurred at ambient temperatures, and an extent of chemical conversion of np to 93% was obtained.

The forth aim of this investigation was to utilize the ene reaction of N-substituted-1,2,4-triazoline-3,5-dione, in which the N-substituent contains a chiral center, to introduce optical activity into polydienes. Since this reaction can occur under very mild conditions, optically active polymers can be made by this novel method, which has not been reported previously. Cis-poly-1,4-butadiene (M W. 200,000 - 300,000), syndiotactic-poly-1,2-butadiene and liquid poly-1,2-butadiene of 85% vinyl contents with M W. 2,000 were selected for this study.

cis-Poly-1,4-butadiene was allowed to react with S-(-)CTD (119) in different solvents at various percentages of conversion, based on molar repeating unit of the polydiene (Scheme XXVIII).

Scheme XXVIII



119 131

Optically active polymer 131 was synthesized at 5%, 10%, 20%, 30%, 50% and 100% of conversion (Table XIX). S-(-)CTD 119 is quite stable in toluene and methylene chloride; therefore, at 5% and up to 30% of conversion, toluene was used as a solvent. At 5% conversion, the reaction was complete in about 8 minutes, and polymer was obtained by precipitation in 95% EtOH. This polymer has a softening point lower than room temperature and therefore is an elastomeric material. At 10% conversion, the reaction was complete in about 30 minutes, and the resulting polymer still has a low softening point. Polymer modified at 20% conversion precipitated from the toluene solution and also is an elastomer with a softening point lower than room temperature.

TABLE XIX

Chemical Conversion of Cis Poly-1 4-Butadiene With S (—) CTU at Room Temperature

Solvent	Reaction Time (Hr)	Feed %	Percentage Incorporation of S-(-) CTU (% N)	T_g[a]
Toluene	0.13	5		(b)
Toluene	0.50	10	10 (0.47)	(b)
Toluene	24	20	18 (0.30)	(b)
Toluene	96	30	35 (12.75)	125
Toluene & DMSO	8	50	43 (11.49)	150
THF & Toluene	24	100	88 (14.51)	163

[a] Rough estimate from standard Fisher-Johns MP

[b] T_g is lower than room temperature

At 30% conversion, the polymer precipitated and apparently does not swell in the solvent, the reaction required a long time to go to completion (disappearance of the deep-pink color). In this case, the resulting polymer lost its elastomeric property and is a brittle solid with a softening point of 125°C

In the case of 50% conversion, it became necessary to add DMSO to keep the polymer swollen enough for the chemical reaction to occur. Although S-(-)CTD 119 slowly decomposes in DMSO, this rate ($k = 2.63 \times 10^{-6}\ s^{-1}$) is small compared to the rate of the desired reaction At 100% conversion, THF was found to be the best solvent, however, to prevent the undesired side reaction (THF and S-(-)CTD), S-(-) CTD 119 was dissolved in toluene and was added dropwise to the solution of the polymer in THF This method yielded a modified optically active polymer in which 89% of the S-(-) CTD was incorporated into the polydiene (as indicated by nitrogen analysis) This polymer is an off-white solid and has a softening point of 163°C

Thus, it can be concluded that the physical properties of the polymers change from secondary crosslinking effects or elasticity at low degrees of conversion (up to 20%) to rigid, amorphous polymers with high softening points at high degrees of conversion Softening points of the new polymers increase as the percentage of conversion increases.

The polymers were characterized by solubility tests, infrared spectroscopy (IR), ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, measurement of intrinsic viscosity [n], and specific rotation $[\alpha]_{\lambda}^{25}$.

The solubility tests were performed by placing a few milligrams of the polymers into small test tubes containing 1 ml of the solvent. The mixture was shaken periodically for about 20 minutes at room temperature. When a clear solution was obtained after this period, the polymer was recorded to be soluble in that solvent. When the polymer remained insoluble after 1 hour in the solvent, the mixture was allowed to stand for several hours and was then re-examined. If no clear solution was obtained, the polymer was recorded as insoluble. A wide variety of solvents was used for the solubility tests (Table XX). Unmodified cis-poly-1,4-butadiene is soluble in benzene, THF, CH_2Cl_2, etc. As the percentage of conversion increased, the polymer became more soluble in more polar solvents. In the cases of 20%, 30% and 50% conversions, it was found that these polymers are only soluble in pyridine. At 100% conversion, the resulting polymer is soluble in polar solvents and in inorganic and organic bases. In general, the introduction of the polar urazole group into a polymer would tend to decrease its solubility in the non-polar solvents. Perhaps the strong hydrogen bonds formed by the urazole pendant groups prevent the hydrating solvent molecules from penetrating the polymer chains.

An IR study gave very convincing evidence both for the incorporation of the urazole moiety and for intra- and intermolecular hydrogen bonding. The polymer modified at 100% is a nice powder, and a KBr pellet was easily prepared (Table XXI). This polymer showed two N-H stretches at 3450 and 3220 cm^{-1}. The first one is due to the free N-H stretching band, and the second one is due to hydrogen bonding. The evidence for such intramolecular hydrogen bonding was also given by

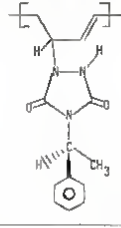
TABLE XX

Solubility of Cis-Poly-1,4-Butadiene Modified with S-(-) CTD

% Conversion	Soluble	Insoluble
0	BZ, Tol, THF, Pyr, CH_2Cl_2	MeOH, DMSO, polar solvents
5	BZ, Tol, CH_2Cl_2, Pyr	DMSO, DMF, ether, alcohol
10	Pyr, DMA, DMF	Tol, 0.1 N KOH, 1.0 N KOH, THF
20	Pyr	Tol, DMA, $CHCl_3$, DMF, 0.1 N KOH, 1.0 N KOH, EtAc, etc.
30	Pyr	"
50	Pyr	"
100	DMSO, THF, CH_2Cl_2, DMF, 0.1 N KOH, 1.0 N KOH	EtOH, acetone, ether, BZ, Tol, CCl_4

TABLE XXI

IR Data for the 100% Conversion of
Cis-Poly-1,4-Butadiene with S-(-) CTD



S-(-) 100% Conversion
White Powder

(KBr)

Infrared Spectroscopy	IR Band cm^{-1} Frequency	Intensities
N-H Stretching (free)	3450	(m, br)
N-H Stretching (H-bonded)	3220	(m, br)
N-H Bending	1500	(w)
C=O Stretching	1765	(s)
	1700	(s)
C-N Stretching	1430	(s)
out of plane C-H aromatic bend	760	(m)
out of plane ring C—C bend	700	(m)

X-ray analysis of model compound 125. The presence of the urazole pendant groups was confirmed by the carbonyl stretching bands which occur as strong bands at 1765 and 1700 cm^{-1}. Also, an out-of-plane C-H aromatic bend at 760 cm^{-1} and an out-of-plane ring C=C bend at 700 cm^{-1} are characteristic vibrational frequencies for the mono-substituted aromatic ring.

The ^1H NMR spectrum (Figure 34) of the 100% modified cis-poly-1,4-butadiene with S-(-) CTD showed a peak at 10.29 ppm, which was assigned to the N-H proton of the urazole moiety. The peak at 7.32 ppm was assigned to the aromatic protons. The other peaks are broad and did not provide a great deal of information about the structure of the polymer.

Although the ^1H NMR spectrum of the modified polymers did not give much structural information, the ^{13}C NMR spectra were found to be very useful. The ^{13}C NMR spectra (Figure 35) of unmodified and modified cis-poly-1,4-butadiene were recorded in $CDCl_3$, Py-d_5 and DMSO-d_6 for comparison. At 5% and 10% conversion, the spectra were taken in $CDCl_3$ and showed small peaks for CH_3, CH, aromatic and carbonyl carbons. In the case of 50% conversion, the solubility is low, and the only solvent found to give a useful spectrum was Py-d_5. At 100% conversion, the modified polymer has very good solubility in DMSO-d_6, and the spectrum gave very useful information about its structure. The assigned peaks are in agreement with the assigned structure.

The intrinsic viscosities [η] (Table XXII) of unmodified and modified cis-poly-1,4-butadiene were measured in pyridine at 30°C by the

Figure 34— ^{1}H NMR (100 MHz) spectrum of the 100% modified cis poly 1,4 butadiene with S-( ) CTP in DMSO-d_6 at 25°C

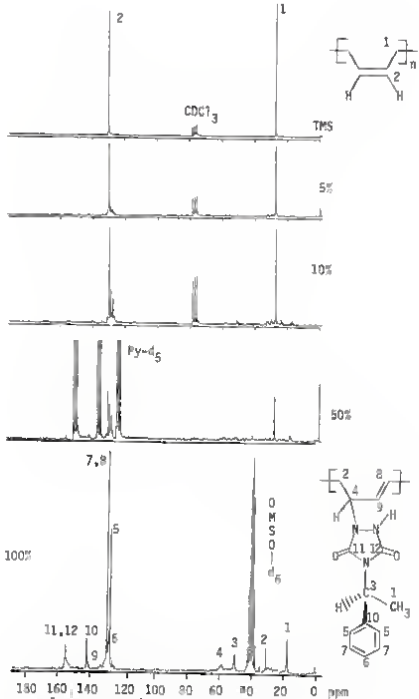


Figure 35— ^{1}H decoupled ^{13}C NMR (25 MHz) spectra of unmodified and modified cis-1,4-polybutadiene with S-(-) CTD in $CDCl_3$ and DMSO-d_6 at 25°C.

TABLE XXII

INTRINSIC VISCOSITIES OF MODIFIED CIS-POLY-1,4-BUTADIENE IN PYRIDINE AT 30°C

% Conversion	[η] dl/g	COC
0[a]	1.87	0.9745
0	1.00	0.9995
10	0.44	0.9829
20	0.29	0.9810
30	0.50	0.9736
50	0.25	0.9995
100[b]	0.15	0.9983

[a] Solvent toluene. [b] Solvent DMF.

dilution method. The [η] of unmodified polymer in pyridine was 1.00 dl/g, whereas that of 10% modified polymer was found to be 0.44 dl/g. In general, the [η] decreases as the percentage of the incorporation of the polar urazole pendent group increases. This is due to the intramolecular interaction between the urazole moiety. This interaction causes the modified polymers to contract and show a drastic change in their molecular sizes.

The optical rotations (α) of modified cis-poly-1,4-butadiene were measured, and specific rotations ($[\alpha]^{25}_{546}$) were calculated (Table XXIII). The $[\alpha]^{25}_{546}$ usually increases as the percentage of conversion increases. Thus, the modified polymers are optically active and have a negative rotation. The $[\alpha]^{25}_{546}$ of model compound 121 in pyridine was found to be -17.2°, and the polymer modified at 100% conversion showed a $[\alpha]^{25}_{546}$ -11.0° in the same solvent. The optical rotations of cis-poly-1,4-butadiene at 100% conversion with S-(-) CTD also were measured in CH_2Cl_2 at different wavelengths and are summarized in Table XXIV.

Syndiotactic-poly-1,2-butadiene (M.P. 90°C) and polybutadiene-85%-1,2- and 15%-1,4- content (M.W. 2,000, liquid) were also modified with S-(-) CTD 119 at 100% conversion (Scheme XXIX). The former was also modified with R-(+) CTD at 100% conversion. As had been demonstrated before with the model compound studies, the reactions are more complicated in this case and presumably lead to a mixture of compounds 132 and 133. Table XXV shows the reaction conditions and results obtained for the modification of 1,2-polybutadiene with S-(-) CTD.

TABLE XXIII

Optical Rotation Measurement of Modified Cis-Poly-1,4-Butadiene

% Conversion	Conc. mg/ml	Solvent	α°	$[\alpha]_{546}^{25}$
0	5.00	Pyridine	0	0
10	5.00	Pyridine	-0.025	-5.1
20	5.10	Pyridine	-0.025	-4.9
30	5.00	Pyridine	-0.041	-8.2
50	5.00	Pyridine	-0.036	-7.2
100	5.00	Pyridine	-0.055	-11.0
100	10.00	THF	-0.115	-11.6

TABLE XXIV

Optical Rotation Measurement of Modified Cis-Poly-1,4-Butadiene With S-(-) CTO at 100% Conversion in CH_2Cl_2 at Different Wavelength (c = 5.0 x 10^{-3} g/ml, ℓ = 1 dec)

λ_{nm}	α°	$[\alpha]_{\lambda}^{25}$
633	-0.094	-18.8
589	-0.111	-22.2
546	-0.131	-26.2
435	-0.222	-44.4
405	-0.260	-52.0

Scheme XXIX

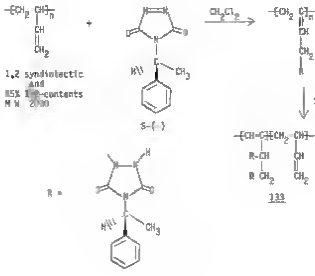


TABLE XXV

Modification of 1,2-Polybutadiene with S-(-) CTD

	1,2-Polybutadiene Syndiotactic	1,2-Polybutadiene 85% Vinyl 1,2-Contents (Liquid)
Reaction Time (Hr)	26	24
Solvent	CH_2Cl_2	CH_2Cl_2
Temperature °C	40	40
Non-Solvent	ether	ether
% Feed	100	100
% Incorporated	91 (14.83)	92 (14.99)
% Yield	75	75
T_s[a] (modified)	185°C	167°C
M.S. (unmodified)	90°C	-

[a] Rough estimate from standard Fisher-Johns M.P.

The reaction solvent in both cases was CH_2Cl_2, but it was necessary to heat the reaction mixture to 40°C for the reactions to occur within a reasonable time period. Ether was found to be a good precipitant, and a 75% yield was obtained after purification. The amounts of S-(-) CTD 119 incorporated in these cases were 91% and 92%, respectively, based on nitrogen analysis. A drastic increase was observed in the softening points of the modified polymers, as expected (Table XXV).

The infrared spectra of the modified poly(1,2-butadiene) gave information similar to the IR spectra of the corresponding modified 1,4-butadienes. The ^1H NMR spectrum showed a downfield peak for the N-H proton of the urazole moiety and a peak at about 7.0 ppm for the aromatic protons. The other peaks are broad and did not give very much information.

The ^{13}C NMR spectrum (Figure 36) of 100% modified syndiotactic poly-1,2-butadiene is more consistent with structure 133. The ^{13}C NMR spectrum of the unmodified polymer is shown also for comparison. The ^{13}C NMR spectrum (Figure 37) of the modified 95%-1,2-polybutadiene is more complicated and is in agreement with a mixture of structures 131 and 133. This is not surprising at all, since poly-1,4-butadiene reacts faster than poly-1,2-butadiene. Therefore, 15% of 1,4- will react first, then the 1,2-structure will react. The ^{13}C NMR spectrum of unmodified 95%-1,2-polybutadiene in $CDCl_3$ is shown for comparison. The ^{13}C NMR data of the modified 1,2-polybutadienes are given in Tables XXVI and XXVII.

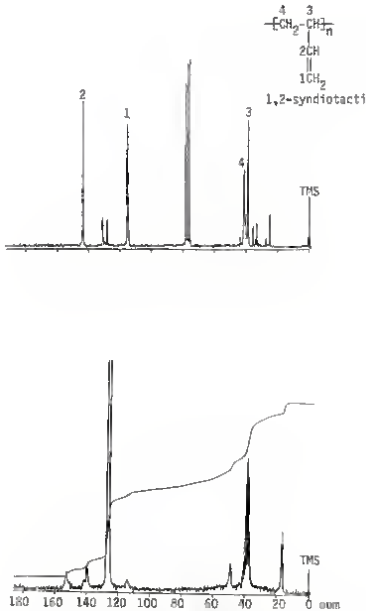


Figure 36 ^{1}H decoupled ^{13}C NMR (25 MHz) spectra of unmodified and modified syndiotactic-poly-1,2-butadiene in $CDCl_3$ and DMSO-d_6, respectively, at 50°C

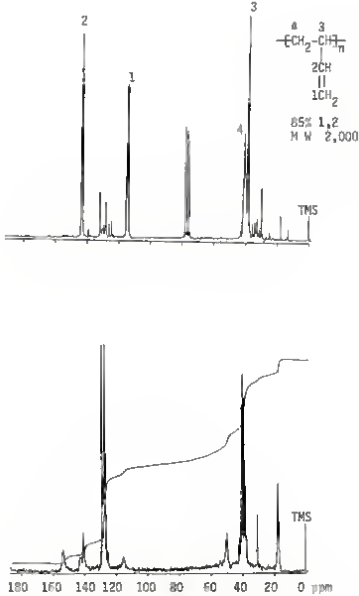
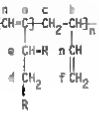


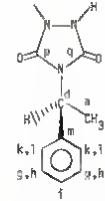
Figure 37. ^{1}H decoupled ^{13}C NMR (25 MHz) spectra of unmodified and modified 85%-poly-1,2-butadiene in $COCl_3$ and DMSO-d_6, respectively, at 25°C.

TABLE XXVI

^{13}C NMR Data[a] for Modified Syndiotactic-Poly-1,2-Butadiene With S-(-) CTD



N =

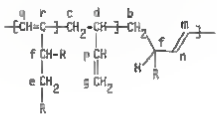


Carbon	Chemical Shift, ppm	Carbon	Chemical Shift, ppm
a	17.13	k	127.96
b & c	Under DMSO-d_6	l	128.20
d	43.69	m	140.34
e	50.08	n	141.22
f	114.95	o	142.19
g	126.11	p	152.62
h	126.40	q	153.06
i	127.08		

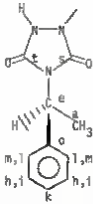
[a] Solvent DMSO-d_6, Int. Ref. DMSO-d_6, 39.5 ppm, Temperature 50°C.

TABLE XXVII

^{13}C NMR Data[a] for Modified 85%-1,2-15%-1,4-Polybutadiene With S-(-) CTO



R =



Carbon	Chemical Shift, ppm	Carbon	Chemical Shift, ppm
a	17.32	l	128.15
b	30.37	m	128.44
c & d	Under DMSO-d_6	n	130.91
e	49.88	o	140.58
f	50.22	p	141.56
g	114.94	q	142.09
h	126.34	r	142.68
i	126.69	s	152.36
k	127.22	t	153.30

[a] Solvent DMSO-d_6, Int. Ref. DMSO-d_6, 39.5 ppm, Temperature 25°C.

Some physical properties of 1,2-polybutadienes modified with S-(-) CTD were studied and are shown in Table XXVIII. In both cases, the modified polymers are white, fluffy powders. The unmodified syndiotactic-poly-1,2-butadiene has $[\eta]$ = 1.38 dl/g in THF. The modified polymer showed $[\eta]$ = 0.35 dl/g in THF. This drastic decrease in $[\eta]$, as was discussed previously, is due to contraction of the polymer chains by intramolecular interaction. The 1,2-modified polymers are optically active and have $[\alpha]_D^{25}$ -20° and -22.8°, respectively, in CH_2Cl_2. The modified polymers are usually soluble in polar solvents like DMSO, THF, DMF, pyridine, etc. and in inorganic and organic bases. They are insoluble in benzene, ether, CCl_4, etc.

The syndiotactic-poly-1,2-butadiene was also modified with R-(+)-CTD, and the polymers have properties similar to the above mentioned modified polymers. They are optically active, and their optical rotations were measured in CH_2Cl_2 at different wavelengths (Table XXIX).

Summary and Conclusions

In the first part of this investigation, it was shown that the methyl urethane derivative of isoeugenol undergoes reaction with PhTD and MeTD. These reactions are exothermic, fast and occur at ambient temperature. These reactions also are stereoselective and lead to only one adduct, namely Diels-Alder-ene adduct. These two reactions served as model reactions for the polymerization study.

After complete characterization and identification of the model compounds, the reactions between bis-triazolinediones and the methyl

TABLE XXVIII

Physical Properties of 100% Modified 1,2-Polybutadienes With S ( ) CTD

	1,2-Polybutadiene Syndiotactic	1,2 Polybutadiene 85% Vinyl 1,2-content
Color	White	White
[η] unmodified dl/g	1.38 (THF, 30°C)	
[η] modified dl/g	0.35 (THF, 30°C)	0.06 (THF 25°C)
$[\alpha]_D^{25}$	20 (C = 1.0 x 10^{-2} g/ml, CH_2Cl_2)	-8.21 (C = 7.92 x 10^{-3} g/ml, THF)
	20 (C = 8.0 x 10^{-3} g/ml, CH_2Cl_2)	-22.6 (C = 1.0 x 10^{-2} g/ml, CH_2Cl_2)
Soluble	CH_2Cl_2, THF, DMSO, DMF, 0.1 N KOH, Pyr,	DMSO, DMF, 0.1 N KOH, CH_2Cl_2, $CHCl_3$
Insoluble	BZ, Tol, ether, CCl_4	Tol, cyclohexane, EtOH, ether, CCl_4

TABLE XXIX

Optical Rotation Measurement of Modified Syndiotactic-Poly-1,2-Butadiene With R-(+) CTD at 100% Conversion in CH_2Cl_2 at Different Wavelengths (C = 5.0 x 10^{-3} g/ml, l = 1 dm)

λ_{nm}	α^a	$[\alpha]_\lambda^{25}$
633	+ 0.098	+ 19.6
589	+ 0.112	+ 22.4
546	+ 0.134	+ 26.8
435	+ 0.223	+ 44.6
405	+ 0.240	+ 48.0

urethane derivative of isoeugenol were investigated. The reactions took place at room temperature and yielded alternating copolymers. From the spectral evidence and comparison with the model compounds, it became clear that these copolymers have Diels-Alder-ene repeating units in their structure. The copolymers are white solids with high thermal stability.

Thus, it can be concluded that isoeugenol reacts rapidly with bis-triazolinediones and yields Diels-Alder-ene copolymers. Therefore, it is potentially a suitable plasticizer for the development of a new elastomeric impression material using a bis-triazolinedione as a crosslinking agent.

In the second part of this research, optically pure triazolinediones were synthesized. These triazolinediones are stable in solvents such as acetone, CH_2Cl_2 and toluene but slowly decompose in solvents such as DMSO, DMF and THF. The pseudo first-order kinetics for such decomposition were studied, and the half-lives of S-(-) CTD in DMF, THF and DMSO were found to be 5.02, 34.10 and 76.20 hours, respectively. In the cases of DMF and DMSO, such decomposition probably occurs via dimerization, but in THF, it reacts with THF via a hydrogen abstraction and addition reaction. The product was isolated and fully characterized. The reaction is not stereospecific and yielded the SR and SS diastereoisomers in about a 50:50 ratio. Evidence for such a product was provided by the ^{13}C NMR study.

Two model compounds were made by reaction of optically pure triazolinedione with olefins and served as models for the polymer modification. An X-ray analysis of a brominated model compound showed

that no racemization had occurred during the course of the seven-step synthesis. It also confirmed the existence of intramolecular hydrogen bonding.

The ene reaction of optically active pure triazolinediona with polybutadiene yielded optically active polymers. The degree of conversion can vary from 5% or lower up to 92%. In the case of 1,4-polybutadiene, reaction occurs at room temperature. The physical properties of the polymers change from secondary crosslinking affects or elasticity at low degrees of conversion (up to 20%), to rigid, amorphous polymers with high softening points at high degrees of conversion. The modified polymers are more soluble in more polar solvents. The intrinsic viscosity of the modified polymers decreases as the percent conversion increases. This is due to intramolecular interaction between the urazole pendant groups. Evidence for such intra- and intermolecular interactions was given by X-ray analysis and an infrared spectroscopy study. For the structural determination, ^{13}C NMR spectroscopy provided very useful information.

From the above, it can be concluded that a wide variety of optically active pure triazolinadionas can be synthesized, and their ene reactions with homopolymers and copolymers containing allylic hydrogen yield optically active polymers with different degrees of conversion. These polymers have different physical properties and potentially can be used as optically active ion-exchange materials if suitably crosslinked.

APPENDIX

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR
S-(-)-4-(α-METHYLBENZYL)-1-(2,3-DIBROMOPROPYL)URAZOLE

L	FO	FC	ALPHA
H=	0, K=	0	
2	995	774	-3.12
4	-58	63	-49.16
6	183	177	0.11
8	1311	1408	-45.06
10	323	430	-2.86
12	1282	1176	-3.09
14	445	516	-3.00
16	428	346	-0.12
18	328	348	-0.12
20	345	338	-2.85
22	488	434	-1.01
24	324	434	-3.49
H=	0, K=	1	
1	788	774	-1.49
3	681	711	-1.53
5	388	389	1.68
7	854	742	1.70
9	578	644	-1.58
11	-20	18	-3.48
13	468	418	1.78
15	348	318	-1.28
17	1242	1208	1.67
19	1262	1138	1.61
21	464	483	-0.22
23	308	322	-1.43
25	548	558	-1.48
27	681	698	-1.49
29	148	122	1.46
31	313	330	1.69
33	778	780	1.67
35	-40	46	1.84
37	492	482	1.52
39	167	198	-1.52
41	348	358	1.53
43	381	368	1.71
45	-101	34	1.83
47	168	182	-1.48
H=	0, K=	2	
0	1668	1715	-3.09
1	61	63	-0.89
2	182	158	-0.93
3	1228	1188	3.00
4	1603	1555	0.0
5	6849	6453	0.08
6	349	382	3.14
7	1278	1268	-0.07
8	1684	1657	3.08
9	1677	1771	-3.14
10	328	352	-0.13
11	852	868	0.10
12	1444	1438	-3.14
13	1428	1402	-3.06
14	418	386	-0.14
15	388	382	-3.08
16	1168	1188	-3.14
17	788	814	0.11
18	143	143	-0.12
19	348	318	-3.08
20	448	348	3.03
21	238	218	0.11
22	378	418	0.08
23	158	168	-0.14
24	-124	188	0.13
H=	0, K=	3	
1	488	488	1.58
3	198	188	1.58

L	FO	FC	ALPHA
3	1178	1318	-1.42
4	384	353	-1.43
5	661	616	-1.48
6	622	614	-1.30
7	338	273	1.25
8	643	576	1.48
9	411	398	1.41
10	182	182	-1.08
11	384	368	-1.48
12	358	352	1.48
13	174	181	1.59
14	664	648	1.63
15	358	358	1.63
16	618	643	-1.44
17	484	51	-1.38
18	188	188	-1.58
19	98	115	-1.58
20	96	84	1.43
21	381	381	1.43
22	388	338	-1.43
23	388	408	-1.42
24	387	388	1.68
H=	0, K=	4	
0	881	1088	-3.08
1	352	368	-3.08
2	318	128	0.15
3	868	843	-1.68
4	631	618	0.07
5	884	837	-3.02
6	768	711	0.09
7	241	241	0.10
8	1478	1484	-3.14
9	477	488	0.02
10	240	254	0.09
11	841	841	0.10
12	1478	1484	-3.14
13	542	542	-3.06
14	843	868	0.09
15	478	467	0.08
16	481	51	-3.04
17	488	488	-3.14
18	448	436	-3.08
19	888	888	-3.09
20	384	384	-3.01
21	438	434	-3.01
22	384	382	3.14
23	388	397	-3.43
24	128	88	0.18
25	148	188	0.03
H=	0, K=	5	
0	488	467	1.44
1	838	867	1.43
2	848	847	1.43
3	888	888	1.43
4	838	818	1.43
5	838	818	1.43
6	838	818	1.43
7	838	818	1.43
8	838	818	1.43
9	838	818	1.43
10	838	818	1.43
11	838	818	1.43
12	838	818	1.43
13	838	818	1.43
14	838	818	1.43
15	838	818	1.43
16	838	818	1.43
17	838	818	1.43
18	838	818	1.43
19	838	818	1.43
20	838	818	1.43
21	838	818	1.43
22	838	818	1.43
23	838	818	1.43
24	838	818	1.43
25	838	818	1.43
H=	0, K=	6	
0	838	818	1.43
1	838	818	1.43
2	838	818	1.43
3	838	818	1.43
4	838	818	1.43
5	838	818	1.43
6	838	818	1.43
7	838	818	1.43
8	838	818	1.43
9	838	818	1.43
10	838	818	1.43
11	838	818	1.43
12	838	818	1.43
13	838	818	1.43
14	838	818	1.43
15	838	818	1.43
16	838	818	1.43
17	838	818	1.43
18	838	818	1.43
19	838	818	1.43
20	838	818	1.43
21	838	818	1.43
22	838	818	1.43
23	838	818	1.43
24	838	818	1.43
25	838	818	1.43
H=	0, K=	7	
0	838	818	1.43
1	838	818	1.43
2	838	818	1.43
3	838	818	1.43
4	838	818	1.43
5	838	818	1.43
6	838	818	1.43
7	838	818	1.43
8	838	818	1.43
9	838	818	1.43
10	838	818	1.43
11	838	818	1.43
12	838	818	1.43
13	838	818	1.43
14	838	818	1.43
15	838	818	1.43
16	838	818	1.43
17	838	818	1.43
18	838	818	1.43
19	838	818	1.43
20	838	818	1.43
21	838	818	1.43
22	838	818	1.43
23	838	818	1.43
24	838	818	1.43
25	838	818	1.43

L	FO	FC	ALPHA
0	393	398	+1.44
1	603	614	+1.32
2	791	749	+1.42
3	178	167	+1.44
4	449	446	+1.47
5	681	723	+1.76
6	704	684	+1.82
7	116	118	+1.84
8	103	97	+1.71
9	884	841	+1.67
10	418	424	+1.74

H=	0.	K=	10
0	167	164	-0.14
1	454	474	-0.15
2	144	131	-0.44
3	146	136	-0.48
4	48	5	-0.48
5	97	104	-0.23
6	144	174	-2.06
7	444	474	-2.44
8	414	444	-2.44
9	764	746	-0.11
10	149	44	-0.23
11	544	514	0.12
12	164	44	3.16

H=	0.	K=	11
1	193	193	-1.44
2	253	223	-1.73
3	104	141	-1.74
4	103	87	-1.34
5	143	13	-0.83
6	144	134	1.70
7	444	147	1.59

H=	1.	K=	0
1	328	888	1.80
2	838	872	2.08
3	1478	1888	-1.82
4	1818	1874	-3.24
5	121	1838	-1.47
6	311	371	1.87
7	482	489	1.84
8	1869	1868	0.08
9	198	248	1.11
10	381	321	-3.82
11	324	488	1.84
12	231	263	0.82
13	444	438	1.87
14	951	984	0.11
15	898	899	-1.84
16	292	299	-1.84
17	88	84	-1.54
18	448	449	-1.41
19	88	98	1.84
20	317	317	-1.80
21	144	137	1.87
22	214	218	-1.42
23	441	412	-3.08
24	183	183	1.84
25	417	438	0.04

H=	1.	K=	1
0	44	44	-0.28
1	432	481	+1.08
2	474	484	-1.27
3	811	861	1.10
4	1681	1611	-2.42
5	353	367	1.36
6	1294	1178	7.84
7	854	906	-0.04

L	FO	FC	ALPHA
8	1078	988	+0.82
9	1163	1148	+0.19
10	884	913	+0.88
11	401	388	2.48
12	418	408	1.28
13	633	681	+1.28
14	478	748	+1.31
15	486	448	+2.04
16	346	388	2.14
17	533	426	2.12
18	311	316	2.61
19	327	317	+2.34
20	398	316	+2.44
21	376	387	0.73
22	338	346	+2.54
23	418	396	2.01
24	478	396	1.13

H=	1.	K=	2
0	1128	1286	1.86
1	1146	1816	-0.77
2	647	516	0.44
3	1267	1166	0.33
4	611	715	-1.01
5	526	557	0.38
6	363	346	0.44
7	646	767	0.66
8	1366	1646	-1.47
9	474	473	-0.81
10	357	463	-7.16
11	667	673	-0.77
12	727	641	1.41
13	365	448	-0.44
14	146	147	0.04
15	216	184	-0.44
16	274	274	0.76
17	446	454	0.37
18	893	883	1.46
19	273	223	1.16
20	422	427	-0.82
21	248	273	0.89
22	327	321	-0.83
23	106	99	-0.91
24	102	21	8.53

H=	1.	K=	3
0	721	788	-1.44
1	1418	1477	-0.89
2	911	937	0.37
3	178	154	0.28
4	497	112	4.42
5	288	284	1.86
6	877	744	-0.47
7	648	683	0.46
8	927	946	1.58
9	714	674	0.16
10	866	778	2.24
11	478	446	0.84
12	895	831	+2.08
13	367	384	-0.14
14	334	307	0.31
15	464	494	0.49
16	963	988	0.88
17	223	216	-0.88
18	348	387	-1.21
19	404	472	0.52
20	676	688	2.88
21	846	851	0.61
22	188	56	-0.66

H=	1.	K=	4

L	FO	FC	ALPHA
0	666	886	+1.47
1	746	727	+2.16
2	882	832	+2.47
3	466	458	+0.76
4	666	644	0.46
5	176	147	2.36
6	446	468	-0.76
7	616	631	-0.62
8	666	611	+2.69
9	446	444	-0.76
10	667	581	0.32
11	111	114	0.63
12	152	146	-1.23
13	551	612	+0.44
14	477	466	+2.13
15	446	481	2.07
16	536	571	-0.60
17	612	606	-1.08
18	158	161	-0.81
19	663	616	-0.16
20	756	757	0.63
21	176	67	0.11
22	336	367	0.19
23	176	208	0.47

H=	1.	K=	5
0	373	368	-1.24
1	466	437	0.46
2	476	471	1.46
3	766	796	0.98
4	666	629	0.83
5	1068	1029	-0.23
6	666	636	+1.17
7	611	579	-0.62
8	746	723	0.68
9	666	648	-0.12
10	199	186	+0.61
11	666	636	-1.13
12	388	389	+2.08
13	466	436	2.31
14	466	434	2.05
15	881	831	0.88
16	467	452	+2.76
17	142	142	+2.18
18	444	474	+2.04
19	181	182	1.26
20	103	84	8.83
21	81	84	+0.41
22	181	177	+0.07

H=	1.	K=	6
0	884	887	1.47
1	226	268	+1.44
2	777	778	0.15
3	867	873	+0.34
4	446	418	0.58
5	381	388	+2.88
6	666	651	0.81
7	407	382	0.17
8	446	446	0.17
9	446	444	0.47
10	146	167	0.27
11	468	438	0.82
12	446	438	+1.04
13	226	219	2.09
14	442	446	1.47
15	666	666	0.66
16	407	43	1.83
17	183	188	1.35
18	681	664	+1.75
19	612	634	+1.42
20	185	182	2.07

L	FO	FC	ALPHA
Xm	1o Xm	7	
0	818	790	1.28
1	387	368	1.48
2	888	867	-4.83
3	405	408	2.00
4	-63	103	-4.22
5	632	627	-0.52
6	422	427	0.18
7	459	456	-2.58
8	132	126	2.68
9	324	324	-0.32
10	752	723	-4.13
11	389	338	-2.63
12	612	482	-0.92
13	411	423	1.21
14	838	848	-1.16
15	329	342	-0.52
16	212	197	-2.22
17	-102	79	-0.00
18	337	338	2.88
19	312	321	1.00
Xm	1o Xm	8	
0	-88	14	0.99
1	387	392	1.51
2	594	548	0.13
3	443	403	1.48
4	-49	188	2.44
5	-188	40	2.77
6	148	279	0.58
7	348	329	1.79
8	188	209	2.77
9	-43	123	-1.62
10	803	804	2.78
11	818	817	0.88
12	-47	32	-1.72
13	348	344	1.31
14	171	79	0.83
15	-101	12	-1.71
16	838	313	-2.71
17	-108	88	1.37
Xm	1o Xm	9	
0	321	278	1.64
1	358	358	1.74
2	482	453	-0.27
3	316	221	-0.73
4	348	337	0.97
5	138	327	2.72
6	285	243	0.08
7	354	288	-1.82
8	838	338	-2.88
9	316	311	1.58
10	388	328	0.16
11	373	313	2.88
12	187	329	-2.22
13	338	352	1.88
14	188	178	-1.38
15	321	843	2.58
Xm	1o Xm	10	
0	-43	28	0.64
1	182	187	-1.88
2	387	885	-1.58
3	388	318	-1.58
4	-88	42	-1.78
5	818	298	-1.88
6	804	438	0.84
7	284	272	0.84
8	-101	74	1.21

L	FO	FC	ALPHA
9	232	201	-2.98
10	138	93	-1.37
11	236	227	1.13
12	188	188	1.42
Xm	1o Xm	11	
0	211	838	-1.80
1	-108	83	2.88
2	373	881	1.36
3	878	881	-2.13
4	171	224	2.89
5	248	348	0.07
6	323	228	1.29
Xm	2o Xm	8	
0	881	884	0.08
1	1137	1194	0.48
2	388	387	0.18
3	1194	1185	0.02
4	213	205	1.0
5	487	488	-0.88
6	784	748	-0.85
7	248	381	1.88
8	882	818	-2.88
9	1137	1138	1.88
10	471	458	1.11
11	181	178	-1.37
12	183	188	0.31
13	853	849	-1.88
14	883	882	0.50
15	418	442	2.23
16	382	885	0.18
17	412	418	-1.13
18	488	93	-1.63
19	122	127	-1.88
20	187	181	-0.88
21	438	888	1.73
22	178	314	-0.88
23	188	84	1.88
Xm	2o Xm	1	
0	881	891	-3.32
1	388	887	-0.42
2	848	847	2.57
3	788	857	0.75
4	112	88	-0.83
5	988	888	0.82
6	88	88	0.00
7	443	488	0.00
8	1063	812	-0.83
9	271	254	1.89
10	838	877	-0.59
11	283	328	0.81
12	888	818	-2.88
13	737	732	-0.98
14	874	878	0.29
15	488	452	-1.19
16	408	468	-2.88
17	485	481	-0.17
18	708	781	1.88
19	176	184	0.08
20	828	826	-0.38
21	178	212	0.37
22	383	345	0.09
23	317	388	1.03
Xm	2o Xm	2	
0	293	288	-2.88
1	884	488	1.82
2	888	811	1.88
3	671	631	0.00

L	FO	FC	ALPHA
4	1434	1388	-1.42
5	231	279	-0.84
6	242	230	-0.12
7	188	136	-1.28
8	1108	878	1.36
9	718	697	1.48
10	211	247	0.88
11	231	247	0.45
12	588	218	1.84
13	188	211	0.28
14	682	678	2.27
15	322	338	2.06
16	413	421	-1.82
17	184	148	1.31
18	182	188	0.88
19	402	488	0.88
20	128	181	1.07
21	-102	132	-1.82
22	214	238	-1.88
23	182	218	-1.98
Xm	2o Xm	3	
0	378	388	-0.89
1	382	288	1.11
2	1087	1038	1.91
3	238	232	2.11
4	888	888	0.82
5	1133	1078	0.82
6	1041	998	0.28
7	188	188	2.84
8	178	171	1.28
9	912	942	-0.03
10	897	402	1.42
11	387	387	0.47
12	303	448	0.43
13	448	892	0.22
14	888	888	0.14
15	788	139	1.78
16	1078	1237	0.12
17	242	242	0.04
18	884	888	0.71
19	118	118	0.84
20	191	212	0.84
21	178	188	0.97
22	108	104	2.22
Xm	2o Xm	4	
0	684	886	0.88
1	381	348	2.12
2	878	888	0.14
3	1188	1188	1.88
4	888	888	0.87
5	487	888	0.24
6	187	124	0.0
7	884	488	0.88
8	171	181	2.17
9	138	148	0.82
10	887	887	1.43
11	787	887	0.72
12	838	888	1.38
13	188	188	0.88
14	888	181	1.18
15	884	218	0.22
16	142	182	2.08
17	885	81	0.92
18	813	228	0.89
19	848	881	0.54
20	217	238	1.82
21	388	211	1.38
22	111	197	1.88

L	FC	FC	ALPHJ
MM	2. KM	6	
0	630	680	0.11
1	638	538	0.68
2	373	662	1.68
3	647	530	0.57
4	762	671	2.47
5	74	122	-1.12
6	537	543	0.28
7	679	670	-0.22
8	420	408	-2.74
9	444	422	-0.55
10	671	644	-0.07
11	702	94	-2.81
12	434	478	-0.16
13	428	69	1.07
14	291	248	-1.47
15	411	394	2.47
16	568	618	1.88
17	58	138	-1.53
18	368	338	0.68
19	486	481	0.68
20	376	370	2.68
21	-168	94	-0.75
MM	2. GM	6	
0	-76	112	0.15
1	380	336	-1.78
2	541	726	0.68
3	363	431	-0.02
4	411	236	0.74
5	526	608	0.50
6	225	284	-0.47
7	218	217	0.68
8	602	820	-1.41
9	153	144	0.75
10	463	636	1.41
11	90	98	-0.36
12	268	308	0.68
13	326	242	-2.58
14	324	324	0.68
15	220	332	-0.75
16	915	454	0.68
17	-162	137	0.38
18	291	230	-1.41
19	134	171	-0.14
MM	2. KM	7	
2	171	135	0.84
3	368	384	-3.84
4	488	416	2.63
5	88	87	-1.88
6	874	856	-1.29
7	134	154	0.68
8	331	358	0.07
9	288	308	0.68
10	176	168	1.18
11	220	253	0.68
12	381	377	-0.43
13	111	113	0.68
14	379	331	0.68
15	684	688	-3.38
16	488	554	2.13
17	228	227	-1.31
18	168	183	-3.94
19	224	228	-0.34
20	188	197	-0.45
MM	2. KM	8	
0	-34	123	-2.75
1	-88	198	1.28
2	186	328	3.12
3	815	621	1.68
4	180	124	-0.61
5	300	264	-1.50
6	49	42	1.28
7	436	434	-1.40
8	302	346	0.33
9	332	301	1.14
10	168	181	0.27
11	262	218	-1.41
12	268	271	-3.48
13	186	231	0.34
14	-102	37	-3.73
15	458	383	1.45
16	-156	108	-2.78
MM	2. KM	2	
0	-80	6	-1.33
1	415	448	2.78
2	317	261	-0.38
3	-93	13	-0.48
4	-98	185	0.43
5	201	668	0.47
6	533	543	-3.75
7	342	319	-0.87
8	312	307	1.47
9	331	180	-0.68
10	-1.03	534	3.08
11	348	871	0.38
12	168	123	2.78
13	173	143	2.65
MM	2. KM	10	
0	-96	181	0.12
1	622	348	-0.41
2	378	397	2.54
3	313	888	-0.12
4	188	885	-1.82
5	-1.08	170	2.98
6	187	134	0.65
7	106	120	0.92
8	347	256	2.44
9	258	206	0.92
10	248	283	-1.78
MM	2. KM	11	
0	228	302	-3.88
1	238	265	0.24
2	-168	78	1.72
MM	3. GM	0	
0	796	894	-1.47
1	1.08	1.08	-3.45
2	882	851	-1.32
3	1.08	1.08	2.78
4	1.08	1.08	-1.78
5	1.08	1.08	2.78
6	1.08	1.08	-2.61
7	917	785	-1.45
8	1.08	1.08	2.78
9	973	389	1.45
10	187	112	0.38
11	471	472	1.71
12	768	845	-0.37
13	667	458	-1.42
14	68	163	0.31
15	1.08	35	-1.38
16	377	381	-3.84
17	84	84	-0.84
18	226	875	-2.58
19	814	342	-1.48
20	281	265	-3.45

L	FC	FC	ALPHK
21	-182	54	1.27
22	214	218	-2.68
MM	2. KM	1	
0	471	472	1.68
1	407	405	0.42
2	744	713	2.68
3	611	587	2.40
4	826	826	-0.82
5	675	698	1.85
6	471	113	0.43
7	181	178	0.41
8	388	353	-1.72
9	559	532	0.46
10	563	557	-0.42
11	1.77	1.77	-0.86
12	335	343	2.65
13	338	338	-1.34
14	387	328	-0.86
15	388	385	-0.25
16	642	588	1.76
17	488	438	1.16
18	183	153	1.14
19	186	188	1.38
20	184	146	-2.42
21	184	227	2.67
MM	3. KM	2	
0	426	282	-1.42
1	848	816	0.37
2	882	872	0.88
3	1.08	1.08	2.68
4	864	826	0.87
5	1.08	1.08	-2.84
6	833	268	-1.38
7	777	777	2.68
8	777	117	0.78
9	448	392	-2.42
10	1.08	1.08	2.68
11	276	275	-0.37
12	1.08	1.08	2.68
13	231	253	0.92
14	1.08	1.08	-0.71
15	172	112	-1.83
16	1.08	1.08	1.41
17	351	348	1.41
18	438	435	-0.98
19	1.08	1.08	-0.21
20	1.08	1.08	2.73
21	1.08	1.08	-2.88

L	FO	FC	ALPHA
20	-106	144	1.78
21	-110	181	-0.36

H=	2. K=	8	
0	470	23	-1.10
1	842	843	2.47
2	328	268	-3.08
3	1629	184	-2.78
4	1382	1218	0.15
5	685	827	-0.65
6	475	131	3.06
7	328	668	-0.37
8	358	336	2.67
9	386	332	-0.36
10	162	134	-0.31
11	145	111	1.11
12	126	178	0.9
13	111	524	2.68
14	211	181	-2.33
15	144	280	-2.42
16	155	329	-0.66
17	197	366	-2.13
18	-106	185	2.91
19	383	346	1.88
20	208	173	2.68

H=	3. K=	8	
0	-78	78	2.81
1	356	330	-0.74
2	758	772	1.11
3	867	863	-0.23
4	863	835	-3.12
5	814	596	-1.82
6	283	549	-1.36
7	454	71	3.46
8	478	460	-0.42
9	438	446	-1.03
10	414	414	0.38
11	244	282	-2.43
12	238	280	-0.38
13	203	226	0.67
14	214	452	0.78
15	146	104	0.78
16	177	134	-0.66
17	-106	130	3.67
18	-104	78	0.38
19	180	83	-1.80

H=	2. K=	9	
0	860	826	1.88
1	655	696	-0.63
2	1384	1372	-0.60
3	287	272	2.63
4	107	205	-2.38
5	305	382	-0.38
6	338	352	2.38
7	1	1	0.0
8	458	438	-2.26
9	357	327	-2.07
10	422	422	0.00
11	233	201	0.48
12	1	1	0.0
13	332	333	-0.42
14	196	196	0.00
15	154	204	-0.26
16	-108	132	-0.76
17	-107	48	0.48

H=	3. K=	7	
0	-84	88	-1.34
1	421	437	1.06

L	FO	FC	ALPHA
2	396	284	-0.22
3	314	313	3.23
4	345	335	-2.66
5	466	291	0.32
6	366	377	2.64
7	376	376	1.47
8	386	324	0.44
9	363	320	-0.12
10	394	331	-3.11
11	324	323	1.87
12	337	331	1.20
13	328	315	-0.10
14	168	166	-0.32
15	211	208	2.70
16	281	284	-2.32

H=	3. K=	9	
0	-88	12	-0.98
1	338	332	-1.75
2	182	172	0.08
3	164	142	1.83
4	374	372	0.01
5	344	328	2.61
6	285	73	0.73
7	203	221	-1.77
8	222	212	0.16
9	170	181	-0.22
10	222	230	-3.66
11	164	166	1.78
12	248	241	-0.92
13	263	218	-1.20

H=	3. K=	10	
0	-88	36	-1.66
1	145	166	2.76
2	186	178	-2.45
3	228	276	-2.09
4	342	338	0.41
5	181	205	-1.05
6	168	216	1.83
7	201	181	-0.88
8	254	254	0.00
9	160	158	-3.16
10	236	232	-0.33

H=	3. K=	10	
0	217	207	-1.44
1	102	82	-0.61
2	238	126	1.83
3	183	166	0.00
4	288	283	2.46
5	233	260	-0.32

H=	0. K=	9	
0	612	688	-3.01
1	1	1	0.0
2	1	1	0.0
3	72	52	0.38
4	672	677	-1.26
5	326	327	0.00
6	317	320	1.74
7	308	316	-3.08
8	633	633	1.67
9	364	364	0.41
10	207	196	1.84
11	488	482	0.00
12	153	153	1.77
13	1	1	0.0
14	431	450	-3.64
15	87	85	-1.68
16	124	121	-1.21
17	653	671	-1.40
18	102	102	2.8

L	FO	FC	ALPHA
17	-58	57	-1.46
18	427	453	-2.01
19	-101	32	1.78

H=	4. K=	1	
0	121	105	-3.58
1	355	354	0.88
2	367	363	0.85
3	369	367	-0.82
4	385	387	-1.71
5	388	381	1.94
6	376	376	-0.11
7	398	398	0.00
8	676	692	-0.61
9	424	426	-0.01
10	324	322	1.21
11	248	248	0.0
12	183	183	1.11
13	51	20	1.34
14	497	513	-0.52
15	146	96	-1.86
16	338	339	-2.12
17	386	389	1.38
18	192	20	0.0
19	173	187	1.88

H=	4. K=	2	
0	146	118	0.87
1	653	643	0.72
2	323	297	-0.93
3	334	327	1.38
4	488	485	-1.81
5	524	524	-2.78
6	102	126	-1.47
7	204	203	0.43
8	122	114	-1.81
9	305	295	-1.12
10	213	213	0.43
11	112	110	0.83
12	334	335	1.10
13	338	385	0.87
14	387	387	0.00
15	387	378	1.73
16	145	111	0.39
17	165	165	1.37
18	81	88	-1.84
19	188	183	-0.12

H=	4. K=	3	
0	338	367	0.16
1	835	838	2.88
2	207	212	-1.44
3	207	212	0.0
4	288	273	1.92
5	252	248	-0.85
6	88	88	1.80
7	1	1	0.0
8	451	452	-0.07
9	334	326	-0.47
10	137	107	0.0
11	449	449	-0.47
12	167	166	1.50
13	386	386	0.86
14	428	432	-1.38
15	331	321	0.0
16	181	187	-1.03
17	153	153	-0.39
18	186	182	-0.24

H=	4. K=	4	
0	521	531	0.18

L	PO	PC	ALPHA
1	-88	148	-1.22
2	278	268	1.18
3	378	371	1.79
4	731	694	0.88
5	321	306	1.06
6	815	824	0.85
7	141	136	1.48
8	694	648	-1.37
9	179	144	1.46
10	416	426	-1.18
11	202	268	0.88
12	287	246	0.99
13	178	148	2.07
14	-98	84	-1.48
15	238	198	1.80
16	288	264	0.99
17	178	148	2.07
18	438	436	-1.38

H= 0, K= 8

L	PO	PC	ALPHA
0	418	468	-8.69
1	-98	18	-0.97
2	888	446	-0.98
3	427	448	0.86
4	432	468	1.27
5	305	322	-0.97
6	139	137	-0.97
7	189	187	1.11
8	671	688	-1.18
9	327	300	1.06
10	388	387	1.84
11	691	678	-0.82
12	188	183	-0.98
13	826	887	-0.98
14	869	886	-0.98
15	-158	108	2.14
16	458	887	-1.79

H= 0, K= 4

L	PO	PC	ALPHA
0	-87	48	-0.25
1	888	867	-0.98
2	188	148	-0.00
3	-78	0	0.00
4	888	446	-1.41
5	228	222	0.00
6	617	228	-0.98
7	379	472	0.00
8	138	191	1.16
9	-98	77	0.00
10	888	888	0.00
11	888	488	0.00
12	488	472	0.00
13	227	283	-1.07
14	198	178	4.11

H= 0, K= 7

L	PO	PC	ALPHA
0	240	261	-2.42
1	129	72	-1.48
2	414	419	1.42
3	47	-112	1.52
4	150	186	-0.71
5	887	888	-0.98
6	178	183	1.11
7	188	184	-0.98
8	107	186	-1.48
9	185	188	-0.74
10			

H= 0, K= 0

L	PO	PC	ALPHA
0	413	418	-3.08

L	PO	PC	ALPHA
1	367	388	1.53
2	231	181	0.00
3	141	154	1.78
4	888	812	0.00
5	101	91	0.21
6	410	388	0.00
7	184	188	1.47
8	194	88	0.00
9	281	816	1.15

H= 0, K= 0

L	PO	PC	ALPHA
0	424	468	2.11
1	188	88	0.00
2	888	888	0.00
3	153	158	1.48

H= 2, K= 0

L	PO	PC	ALPHA
1	485	81	1.58
2	888	883	-1.01
3	228	231	1.09
4	421	428	1.04
5	137	77	1.77
6	227	248	1.08
7	88	111	1.04
8	84	100	1.48
9	181	182	1.00
10	881	818	0.00
11	88	88	0.77
12	236	243	1.08
13	418	287	1.48
14	888	888	0.00
15	188	188	1.40
16	188	83	1.40

H= 4, K= 1

L	PO	PC	ALPHA
0	406	101	-1.04
1	418	428	1.08
2	348	325	1.48
3	888	888	0.00
4	887	886	1.42
5	887	886	0.00
6	88	42	0.11
7	874	818	0.00
8	183	188	1.48
9	888	888	0.00
10	888	888	1.07
11	888	888	0.00
12	188	88	0.00
13	234	288	0.00
14	182	88	0.00
15	888	888	0.00
16	888	888	0.00
17	888	888	0.00
18	888	888	0.00
19	888	888	0.00
20	888	888	0.00
21	888	888	0.00
22	888	888	0.00
23	888	888	0.00
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25	888	888	0.00
26	888	888	0.00
27	888	888	0.00
28	888	888	0.00
29	888	888	0.00
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37	888	888	0.00
38	888	888	0.00
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H= 0, K= 0

L	PO	PC	ALPHA
0	-86	0	-0.03
1	258	258	1.18
2	357	363	-1.18
3	140	148	-1.07
4	145	142	-1.08
5	182	220	-1.01
6	686	657	1.74
7	237	274	1.07
8	181	183	1.14
9	181	183	-0.00
10	-88	182	0.74
11	188	183	0.00
12	-88	34	0.17
13	188	88	0.00
14	337	382	-1.31

H= 2, K= 0

L	PO	PC	ALPHA
0	348	397	1.01
1	-81	118	0.18
2	188	113	0.00
3	181	38	1.17
4	-88	178	0.00
5	-88	84	1.48
6	188	188	1.07
7	188	188	0.00
8	383	388	-0.38
9	188	142	0.00
10	301	318	-1.44
11	188	257	0.00
12	-188	172	-1.88
13	188	88	2.77

H= 2, K= 1

L	PO	PC	ALPHA
0	248	258	1.08
1	284	284	1.18
2	284	114	2.18
3	188	188	1.40
4	324	324	1.87
5	88	78	0.00
6	311	318	-1.27
7	188	88	0.00
8	188	181	1.28
9	188	188	1.33
10	323	388	-1.33
11	878	881	1.87

H= 4, K= 0

L	PO	PC	ALPHA
0	-88	88	-1.47
1	472	887	0.71
2	-88	88	0.00
3	848	832	3.04
4	188	88	0.00
5	148	188	0.00
6	-88	88	0.07
7	188	88	0.00

H= 0, K= 7

L	PO	PC	ALPHA
0	227	281	-1.41
1	-58	104	-0.12
2	181	885	0.38
3	-181	178	1.01
4	188	181	1.78

H= 0, K= 0

L	PO	PC	ALPHA
0	-53	71	-3.10
1	184	188	1.01
2	184	188	+0.04
3	388	387	-1.40

L	FC	FC	ALPHA	L	FC	FC	ALPHA	L	FC	FC	ALPHA
6	137	13	-8.43	7	286	310	-6.76				
8	157	116	1.74	8	-101	128	-5.60	0	256	288	0.10
8	462	332	0.17					1	187	232	-2.91
7	-98	126	1.20	MB	0. K=	2		2	316	336	2.81
7	-47	11	1.68					3	-65	134	2.27
8	173	121	-1.43	0	188	179	0.10	4	-97	94	0.69
				1	180	228	-3.08	5	-85	73	0.08
MB	0. K=	1		8	186	221	-4.74	6	186	187	0.06
				2	-98	88	0.00				
0	-98	98	0.09	4	-97	108	0.10	MB	0. K=	6	
1	182	178	1.35	8	-98	128	-1.61				
2	238	281	-0.17	8	-48	42	0.27	0	283	238	-3.42
3	335	333	1.88	7	288	268	-0.84	1	-188	146	-0.72
6	-47	84	-0.20	8	218	229	-1.94	2	-188	84	0.40
8	313	342	-2.68								
4	148	202	-0.12	MB	0. K=	3					

REFERENCES

1. B.T. Gillis, "1,4-Cycloaddition Reactions," J. Hamer, Ed., Academic Press, New York, 1967, p. 143-177.

2. O. Diels, J.H. Blom, and W. Kohl, Annalen, 443, 243 (1925).

3. J. Thiele and O. Stange, Liebigs Ann., 283, 1 (1894).

4. J. Stolle, Ber. Dtsch. Chem. Ges., 45, 273 (1912).

5. R.C. Cookson, S.S.H. Gilani, and I.O.R. Stevens, Tetrahedron Lett., 14, 615 (1962).

6. B.T. Gillis and J.D. Hagarty, J. Org. Chem., 32, 330 (1967).

7. J. Sauer and B. Schroder, Ber., 100, 678 (1967).

8. F. Yoneda, K. Suzuki, and Y. Nitta, J. Am. Chem. Soc., 88, 2328 (1967).

9. J.C. Stickler, Ph.D. Dissertation, University of Illinois, 1971.

10. J.C. Stickler and W.H. Pirkle, J. Org. Chem., 31, 3444 (1966).

11. J.A. Moore, R. Muth and R. Sorace, J. Org. Chem., 39, 3799 (1974).

12. M.G. deAmezua, M. Yora-Tamaya, and J.L. Soto, Tetrahedron Lett., 2407 (1970).

13. J.E. Herweh and R.M. Fantazier, Tetrahedron Lett., 2101 (1973).

14. J.M. Cinnamon and K. Weiss, J. Org. Chem., 26, 2644 (1961).

15. K. Alder and T. Hohle, Ber., 76, 54 (1943).

16. B.T. Gillis and F.A. Daniher, J. Org. Chem., 27, 4001 (1962).

17. B. Franzus and J.K. Sunidge, J. Org. Chem., 27, 1951 (1962).

18. B.T. Gillis and P.E. Beck, J. Org. Chem., 27, 1947 (1962).

19. B.T. Gillis and P.E. Beck, J. Org. Chem., 28, 3177 (1963).

20. J.J. Tufariello, T.F. Mich, and P.S. Millen, Tetrahedron Lett., 2293 (1966).

21. F. Yoneda, K. Suzuki, and Y. Hitta, J. Org. Chem., 32, 727 (1967).

22. E. Fahr and H. Lind, Angew. Chem. Int. Ed., 5, 372 (1966).

23. J.E. Herweh and R.M. Fantazier, Tetrahedron Lett., 2101 (1968).

24. J. Sauer, Angew. Chem., Int. Ed. Engl., 6, 16 (1967).

25. W.H. Pirkle and J.C. Stickler, Chem. Comm., 760 (1967).

26. M.E. Burrage, R.C. Cookson, S.S. Gupte, and I.D.R. Stevens, J. Chem. Soc. Perkin II, 1325 (1975).

27. S.S.H. Gilani and O.J. Trigole, J. Org. Chem., 31, 2397 (1966).

28. A.J. Solo, H.S. Sachdev, and S.S.H. Gilani, J. Org. Chem., 30, 769 (1965).

29. D.G. Farnum and J.P. Snyder, Tetrahedron Lett., 3861 (1965).

30. C.M. Anderson, J.E. Bremmer, I.W. McCay, and R.N. Warrener, Tetrahedron Lett., 1255 (1968).

31. A.G. Anastassiou and R.P. Celluca, Tetrahedron Lett., 911 (1970).

32. D.M. Lemal and J.P. Lokensgard, J. Am. Chem. Soc., 88, 5934 (1966).

33. H.H. Inhoffen, Ann., 508, 81 (1934).

34. A. VanDerGen, J. Lakeman, M.A.M.P. Gras, and H.O. Huisman, Tetrahedron, 20, 2521 (1964).

35. R.C. Cookson, S.S.H. Gilani, and I.D.R. Stevens, J. Chem. Soc. (C), 1906 (1967).

36. A.B. Evnin, R.O. Miller, and G.R. Evaneya, Tetrahedron Lett., 5863 (1968).

37. R. Hnissgen, W.E. Konz, and V. Schnegg, Angew. Chem. Int. Ed. Engl., 11, 715 (1972).

38. A.B. Evnin, D.R. Arnold, L.A. Karnischky, and E. Strom, J. Am. Chem. Soc., 92, 6218 (1970).

39. A.B. Evnin and D.R. Arnold, J. Am. Chem. Soc., 90, 5330 (1968).

40. V.T. Bandurco and J.P. Snyder, Tetrahedron Lett., 4643 (1969)

41. (a) A. Ladenburg, Chem. Ber., 2, 140 (1869)
(b) T.J. Katz and N. Acton, J. Am. Chem. Soc., 95, 2738 (1973).

42. M. Heyman, V.T. Bandurco, and J.P. Snyder, Chem. Commun., 297 (1971).

43. W. Adam, O. Delucchi, and I. Ervin, Angew. Chem., Int. Ed. Engl., 18, 468 (1979).

44. E.K. VonGustorf, O.V. White, B. Kim, O. Hess, and J. Leitich, J. Org. Chem., 35, 1155 (1970).

45. K. Alder, F. Pascher, and A. Schmitz, Ber. Dtsch. Chem. Ges., 76, 27 (1943).

46. (a) R.B. Woodward and A. Hoffman, Angew. Chem., 81, 797 (1969).
R.B. Woodward and A. Hoffman, Angew. Chem., Int. Ed. Engl., 8, 781 (1969).
(b) K.N. Houk, Acct. Chem. Res., 8, 361 (1975)
(c) A. Wasserman, "Diels-Alder Reaction," Elsevier Pub. Co., New York, 1966.

47. O.S. Glass, R.S. Boikess, and S. Winstein, Tetrahedron Lett., 939 (1966).

48. H.M.R. Hoffmann, Angew. Chem., Int. Ed. Engl., 8, 556 (1969).

49. S. Dal and W.R. Dolbiar, Jr., J. Am. Chem. Soc., 94, 3953 (1972).

50. D.J. Pasto and A.F.T. Chen, Tetrahedron Lett., 2995 (1972).

51. B. Saville, Chem. Commun., 635 (1971).

52. C.A. Seymour and F.D. Greene, J. Am. Chem. Soc., 102, 6384 (1980).

53. G.B. Butler, L.J. Guilbault, and S.R. Turner, Polymer Lett., 9, 115 (1971).

54. S.R. Turner, L.J. Guilbault, and G.B. Butler, J. Org. Chem., 36, 2838 (1971).

55. K.B. Wagener, S.R. Turner, and G.B. Butler, J. Org. Chem., 37, 1454 (1972).

56. K.B. Wagener and G.B. Butler, J. Org. Chem., 38, 3070 (1973).

57. K.A. Matyjaszewski, K.B. Wagener, and G.B. Butler, Polymer Lett., 17, 129 (1979).

58. K.A. Matyjaszewski, K.B. Waganar, and G.B. Butler, Polymer Latt., 17, 65 (1979).

59. S. Ohashi, K.W. Laong, K. Matyjaszewski, and G.B. Butler, J. Org. Chem., 45, 3467 (1980).

60. S. Ohashi and G.B. Butler, J. Org. Chem., 45, 3472 (1980).

61. A.G. Williams and G.B. Butler, Polymer Lett., 18, 313 (1980).

62. A.G. Williams and G.B. Butler, J. Org. Chem., 45, 1232 (1980).

63. S. Ohashi, W.E. Ruch, and G.B. Butler, J. Org. Chem., 46, 614 (1981).

64. R.C. Cookson, I.D.R. Stevens, and C.T. Watts, Chem. Commun., 744 (1966).

65. R. Ahmed and J.P. Anselme, Can. J. Chem., 50 (11), 1778 (1972).

66. K.H. Koch and E. Fahr, Angew. Chem., Int. Ed. Engl., 9, 634 (1970).

67. Merck & Co., Inc., "Deuteratad NMR Solvents -- Handy Rafarenca Data," Merck & Co., Inc., Quabac, 1978.

68. A.J. Gordo and R.A. Ford, "The Chemist's Companion. A Handbook of Practical Data, Techniques and Rafarencas," John Wiley & Sons, New York, 1972.

69. R.C. Cookson, S.S.H. Gilani, I.D.R. Stevens, and C.T. Watts, Org. Synth., 51, 121 (1971).

70. G. Zinner and W. Daucker, Arch. Pharm., 294, 3701 (1961).

71. Chemical Abstracts 81:120283p (1974).

72. K.O. Waganar, Ph.D. Dissertation, University of Florida, 1973.

73. L.F. Fieser and M. Fieser, "Reagents for Organic Synthesis," John Wiley and Sons, New York, 1967, p. 1066.

74. S.R. Turnar, Ph.D. Dissertation, University of Florida, 1971.

75. V.F. Kolomiets, R.A. Grachava, V.M. Potapov, and A.L. Samusanke, J. Org. Chem. USSR, 854 (1980).

76. L.A. Paquatte and R.F. Doahnar, Jr., J. Org. Chem., 45, 5105 (1980).

77 K B. Wagener, S R Turner, and G B Butler, Polym. Lett., 10, 805 (1972)

78. (a) S.B. Needleman and M C C Kuo, Chem. Rev., 62, 414 (1962) (b) K. Alder and R Schmitz-Josten, Ann., 595, 1 (1955).

79. Y C. Lal, Ph D. Dissertation, University of Florida, 1980

80. J.W. Baker and D N Bailey, J Chem Soc., 4649, 4652, 4663 (1957).

81. J W. Baker, M.M. Davies, and J. Gaunt, J. Chem. Soc., 24 (1944)

82. J W Baker and J B Goldsworth, J. Chem Soc., 713 (1947).

83. J.W. Baker and J. Gaunt, J Chem. Soc., 9, 19, 27 (1949).

84. H. Wamhoff and K. Wald, Chem Ber., 110, 1699 (1977).

85 The X-ray diffraction analysis was performed by Dr H. Aghabozorg and Dr. G J Palenik, Center for Molecular Structure and Department of Chemistry, University of Florida, Gainesville, Florida

86 B. Fuchs, "Topics in Stereochemistry," E L. Eliel and M.L. Allinger, Eds., John Wiley & Sons, 1978, Vol. 10.

87. D.V. Naik and G.J. Palenik, Crystallogr., Sect B, 30, 2396 (1974).

88. C.S. Marvel, R.L. Frank, and E Prill, J. Am. Chem. Soc., 65, 1647 (1943).

89. C.S Marvel and C.G. Overberger, J. Am. Chem. Soc., 68, 2106 (1946)

90. C G. Overberger and L.C. Palmer, J. Am. Chem. Soc., 78, 666 (1956).

91. N Beredjick and C. Schuerch, J. Am Chem Soc., 80, 1933 (1958).

92. G J Schmitt and C. Schuerch, J. Polym Sci., 45, 313 (1960).

93. N. Yamaguchi and Y Minoura, J. Polym Sci., Part A-1, 8, 929 and 1467 (1970).

94 F. Ciardelli and E Menneagli, J Polym Sci., Polym. Symp., 62, 143 (1978).

95 F. Ciardelli, E. Chiellini, C Carlini, and R. Nacci, Prepr. Paper Nat. Meet. Am. Chem. Soc., Polym. Div., 17, 188 (1976).

96. F. Ciardelli, E. Chiellini, C. Carlini, and M. Aglietto, Pure & Appl Chem , 52, 1857 (1980)

97. Y. Okamoto, K. Suzuk,and H. Yuki, J. Polym. Sci., Polym. Chem Ed., 18, 3043 (1980).

98. R.N. Majumdar, C. Carlini,and C. Bertucci, Makromol. Chem , 183, 2047 (1982)

99. F. Fetter, 'Chemical Reactions of Polymers," Wiley-Interscience, New York, 1964

100. A.G. Williams and G.B. Butler, J. Polym. Sci., Polym. Chem. Ed., 17, 1117 (1979)

101. K.W. Leong and G.B. Butler, J. Macromol. Sci.-Chem , A14 (3), 287 (1980)

102. T.C.S. Chen and G.B. Butler, J. Macromol. Sci.-Chem., A16 (3), 757 (1981).

BIOGRAPHICAL SKETCH

Shadpour Esteleky Mallakpour was born on June 4, 1953, in Lashtenesha, Rasht, Gilan, Islamic Republic of Iran. He was a 1974 graduate of Ahzadegan High School, Rasht, I.R. Iran. The author received the B.S. degree in chemistry from the Shaid Beheshti University, Tehran, I.R. Iran, in 1975. He served two semesters as a laboratories instructor in that university. In 1976, he came to the United States and entered Eastern Michigan University, Ypsilanti, Michigan, where he received the M.S. degree in organic chemistry in 1978. After spending one year at Wayne State University, Detroit, Michigan, he joined the Department of Chemistry at the University of Florida.

While working toward the degree of Doctor of Philosophy in organic polymer chemistry, Mr. Mallakpour served as a teaching and research assistant in the Department of Chemistry. He received the DuPont Teaching Award in 1981, and a Graduate School teaching award in 1982. He has presented two research papers at ACS meetings, in Jacksonville, Florida, in 1982, and in Charlotte, North Carolina, in 1983. He has acted as the chairman of the polymer chemistry seminar program since 1982.

Mr. Mallakpour was married to Mina Pourmojib in December, 1983. The author is a member of the American Chemical Society.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

George B. Butler
George B. Butler, Chairman
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Wallace S. Brey, Jr.
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

William R. Dolbier, Jr.
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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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